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Electronic Supplementary Information (ESI)

Proline Catalyzed Sequential α-Aminooxylation or -Amination/Reductive Cyclization of *o*-Nitrohydrocinnamaldehydes: A High Yield Synthesis of Chiral 3-Substituted Tetrahydroquinolines

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1. General information:

Solvents were purified and dried by standard procedures before use. Optical rotations were measured using sodium D line on a JASCO-181 digital polarimeter. ^{1}H NMR and ^{13}C NMR spectra were recorded on Brucker AC-200 spectrometer unless mentioned otherwise. Elemental analysis was carried out on a Carlo Erba CHNS-O analyzer. IR spectra were recorded on a Perkin-Elmer model 683 B and absorption is expressed in cm^{-1}. Purification was done using column chromatography (230-400 mesh).

2. Experimental section

A general experimental procedure for the preparation of (*R*)-1,2,3,4-tetrahydro-6,7-dialkyloxyquinolin-3-ol (5a-e)

To a stirred solution of *o*-nitrohydrocinnamaldehyde **4a-e** (6 mmol) and PhNO (6 mmol) in DMSO (20 mL), L-proline (20 mol%) was added at 25 ºC and allowed to stir for 20 min. After completion of reaction, as indicated by the change in color from green to yellow, large excess (100 mL) of diethyl ether was poured into the reaction mixture and stirred for additional 10 min. The combined organic mixture was washed with H_2O (5 x 20 mL). The organic layer was separated and aqueous layer was extracted with diethyl ether (2 x 50 mL). Combined organic layers were washed with brine (5 x 50 mL), dried over anhydrous Na_2SO_4 and concentrated under reduced pressure to give the crude product. The crude α-aminooxylated aldehyde was dissolved in MeOH (20 mL) and to this mixture 10% Pd/C (5 wt%) was added. The reaction mixture was then stirred at 25 ^{o}C for additional 6 h. After the completion of reaction (monitored by TLC), it was filtered through celite and the solvent evaporated under reduced pressure. Chromatographic purification of the crude product [flash silica gel (230-400 mesh) and pet. ether:EtOAc: Et_3N (60:38:2)] gave the pure (*R*)-tetrahydroquinolin-3-ol derivatives **5a-e**.

(*R*)-1,2,3,4-Tetrahydroquinolin-3-ol (5a)

Yield: 71% (635 mg); Gum; $[\alpha]^{D}_{25}$ +12.3 (*c* 1, $CHCl_3$); 96% ee from **HPLC analysis**; Column: Chiracel OD-H (250 x 4.6 mm), mobile phase: isopropyl alcohol/n-hexane (10/90), wavelength: 254 nm, flow rate: 0.5 mL/ min, conc.: 1.5mg/mL, injection vol.: 10µL, retention time: 30.07 min (-)-isomer, 33.89 min (+)-isomer; **IR** ($CHCl_3$): υ_{max} 753, 1312, 1500, 1604, 3370, 3413 cm^{-1}; **^{1}H NMR** (200 MHz, $CDCl_3$): δ 2.35 (br s, 1H), 2.76 (dd, *J* = 3.7, 16.5 Hz, 1H), 3.01 (dd, *J* = 4.3, 16.9 Hz, 1H), 3.26-3.38 (m, 2H), 4.21-4.29 (m, 1H), 6.53 (d, *J* = 9.0 Hz, 1H), 6.65 (dt, *J* =

1.1, 7.5 Hz, 1H), 6.97-7.05 (m, 2H); **^{13}C NMR** (50 MHz, $CDCl_3$): δ 35.3, 47.5, 63.2, 114.1, 117.9, 118.7, 126.9, 130.4, 143.5; **ESIMS** (*m*/*z*) 150 $[M+H]^+$; **HRMS** (ESI) calcd for $C_9H_{11}NO$ $[M+H]^+$ 150.0919; found: 150.0910.

(*R*)-1,2,3,4-Tetrahydro-6,7-dimethoxyquinolin-3-ol (5b)

Yield: 76% (954 mg); Gum; $[\alpha]^D_{25}$ +27.1 (*c* 1.26, $CHCl_3$); 98% ee from **HPLC analysis**; Column: Chiracel OD-H (250 x 4.6 mm), mobile phase: isopropyl alcohol/n-hexane (20/80), wavelength: 254 nm, flow rate: 0.5 mL/ min, conc.: 1.5mg/mL, injection vol.: 10µL, retention time: 34.54 min (-)-isomer, 40.99 min (+)-isomer; **IR** ($CHCl_3$): υ_{max} 756, 1217, 1464, 1519, 3456 cm^{-1}; **^{1}H NMR** (200 MHz, $CDCl_3$): δ 2.71 (dd, *J* = 3.9, 16.5 Hz, 1H), 2.85-3.00 (m, 1H), 3.19-3.22 (m, 2H), 3.78 (s, 3H), 3.79 (s, 3H), 4.15-4.23 (m, 1H), 6.12 (s, 1H), 6.50 (s, 1H); **^{13}C NMR** (50 MHz, $CDCl_3$): δ 34.7, 47.6, 55.6, 56.4, 63.3, 99.8, 110.5, 114.2, 136.7, 142.2, 148.0; **ESIMS** (*m*/*z*) 210 $[M+H]^+$; **HRMS** (ESI) calcd for $C_{11}H_{15}NO_3$ $[M+H]^+$ 210.1130; found: 210.1108.

(*R*)-5,6,7,8-Tetrahydro-[1,3]dioxolo[4,5-*g*]quinolin-7-ol (5c)

Yield: 75% (869 mg); Gum; $[\alpha]^D_{25}$ +28.2 (*c* 1, $CHCl_3$); 94% ee from **HPLC analysis**; Column: Chiracel OD-H (250 x 4.6 mm), mobile phase: isopropyl alcohol/ n-hexane (20/80), wavelength: 254 nm, flow rate: 0.5 mL/ min, conc.: 1.5mg/mL, injection vol.: 10µL, retention time: 27.20 min (-)-isomer, 30.60 min (+)-isomer; **IR** ($CHCl_3$): υ_{max} 1037, 1215, 1484, 2853, 2924, 3355 cm^{-1}; **^{1}H NMR (**200 MHz, $CDCl_3$): δ 2.16 (br s, 2H), 2.65(dd, *J* = 3.5, 16.7 Hz, 1H), 2.92 (dd, *J* = 4.2, 16.7 Hz, 1H), 3.21-3.23 (m, 2H), 4.17-4.25 (m, 1H), 5.82 (s, 2H), 6.15 (s, 1H), 6.48 (s, 1H); **^{13}C NMR** (50 MHz, $CDCl_3$): δ 35.1, 47.5, 63.1, 96.4, 100.1, 109.5, 110.6, 137.9, 139.9, 146.1; **ESIMS** (*m*/*z*) 194 $[M+H]^+$; **Anal.** Calcd for $C_{10}H_{11}NO_3$ requires C, 62.17; H, 5.74; N, 7.25; found C, 62.11; H, 5.81; N, 7.30%.

(*R*)-7-(Cyclopentyloxy)- 6-methoxy-1,2,3,4-tetrahydroquinolin-3-ol (5d)

Yield: 72% (1.14 g); Gum; $[\alpha]^{D}_{25}$ +25.7 (*c* 1, $CHCl_3$); 96% ee from **HPLC analysis**; Column: Chiracel OD-H (250 x 4.6 mm), mobile phase: isopropyl alcohol/ n-hexane (50/50), wavelength: 254 nm, flow rate: 0.5 mL/ min, conc.: 1.5mg/mL, injection vol.: 10µL, retention time: 10.23 min (-)-isomer, 11.19 min (+)-isomer; **IR** ($CHCl_3$): υ_{max} 769, 1217, 1456, 1504, 2927, 3402 cm^{-1}; **^{1}H NMR** (200 MHz, $CDCl_3$): δ 1.55-1.83 (m, 8H), 2.72 (dd, *J* = 3.5, 16.5 Hz, 1H), 2.91-2.99 (m, 3H), 3.21-3.23 (m, 2H), 3.76 (s, 3H), 4.16-4.23 (m, 1H), 4.59-4.65 (m, 1H), 6.11 (s, 1H), 6.52 (s, 1H); **^{13}C NMR** (50 MHz, $CDCl_3$): δ 23.5, 32.4, 34.7, 47.6, 55.5, 63.3, 81.4, 99.7, 110.4, 119.1, 137.7, 139.7, 149.5; **ESIMS** (*m*/*z*) 264 $[M+H]^+$; **Anal.** Calcd for $C_{15}H_{21}NO_3$ requires: C, 68.42; H, 8.04; N, 5.32; found: C, 68.38; H, 8.10; N, 5.39%.

(*R*)-7-(*tert*-Butyldiphenylsilyloxy)-6-methoxy-1,2,3,4-tetrahydroquinolin-3-ol (5e)

Yield: 70% (1.82 g); Gum; $[\alpha]^{D}_{25}$ +21.3 (*c* 1, $CHCl_3$); 99% ee from **HPLC analysis**; Column: Chiracel OD-H (250 x 4.6 mm), mobile phase: isopropylalcohol/ n-hexane (2.5/97.5), wavelength: 254 nm, flow rate: 0.5 mL/ min, conc.: 1.5mg/mL, injection vol.: 10uL, retention time: 17.10 min (-)-isomer, 19.44 min (+)-isomer; **IR** ($CHCl_3$): υ_{max} 758, 1226, 1517, 2856, 2929, 3392 cm^{-1}; **^{1}H NMR** (200 MHz, $CDCl_3$): δ 1.10 (s, 9H), 2.59 (dd, *J* = 3.9, 14.5 Hz, 1H), 2.86 (dd, *J* = 3.7, 14.3 Hz, 1H), 3.03-3.51 (m, 2H), 3.51 (s, 3H), 4.08-4.16 (m, 1H), 5.90 (s, 1H), 6.42 (s, 1H), 7.31-7.39 (m, 6H), 7.69-7.73 (m, 4 H); **^{13}C NMR** (50 MHz, $CDCl_3$): δ 19.8, 26.7, 29.7, 35.1, 47.6, 56.7, 63.5, 107.0, 116.0, 127.5, 129.6, 133.7, 135.4, 137.3, 143.7, 144.5; **ESIMS** (*m*/*z*) 434 $[M+H]^+$; **Anal.** Calcd for $C_{26}H_{31}NO_3Si$ requires C, 72.02; H, 7.21; N, 3.23; found C, 72.09; H, 7.18; N, 3.27%.

A general experimental procedure for the preparation of (*R*)-1,2,3,4-tetrahydro-6,7-dialkyloxyquinolin-3-amine (6a-e)

To a stirred solution of nitro hydrocinnamaldehyde **4a-e** (5.5 mmol) and DIAD (5 mmol) in CH_3CN (10 mL), L-proline (20 mol %) was added at 0 ºC and allowed to stir for 3 h. After completion of reaction, as indicated by the disappearance of yellow color, was added MeOH (30 mL) and 10% Pd/C (5 wt%). The reaction mixture was then stirred at 25 ^oC for additional 12 h under H_2 atmosphere (1 atm.). After the completion of reaction (monitored by TLC), it was filtered through celite and the solvent evaporated under reduced pressure. Chromatographic purification of the crude product over flash silica gel (230-400 mesh) and pet. ether:EtOAc gave the pure (*R*)-tetrahydroquinolin-3-amines **6a-e**.

(*R*)-Diisopropyl 1-(1,2,3,4-tetrahydroquinolin-3-yl)hydrazine-1,2-dicarboxylate (6a)

Yield: 82% (1.37 g); gum, $[\alpha]^D_{25}$ -720 (*c* 0.8, $CHCl_3$); 90% ee from **HPLC analysis**; Column: Chiracel OD-H (250 x 4.6 mm), mobile phase: isopropyl alcohol/n-hexane (5/95), wavelength: 254 nm, flow rate: 0.5 mL/ min, conc.: 1.5 mg/mL, injection vol.: 10µL, retention time: 31.73 min (-)-isomer, 34.6 min (+)-isomer; **IR** ($CHCl_3$): 1107, 1180, 1230, 1246, 1306, 1375, 1408, 1511, 1711, 1721, 2932, 2981, 3298 cm^{-1}; **^{1}H NMR** (200 MHz, $CDCl_3$): δ 1.23-1.28 (m, 12H), 2.97-3.47 (m, 4H), 4.62(brs, 1H), 4.94-5.00 (m, 2H), 6.37(brs, 1H), 6.48 (d, *J* = 7.4 Hz, 1H), 6.61 (t, *J* = 7.2 Hz, 1H), 6.96 (m, 2H) **^{13}C NMR** (50 MHz, $CDCl_3$): δ 21.8, 21.9, 30.0, 44.5, 51.0, 69.7, 70.1, 96.0, 113.9, 117.4, 119.5, 126.8, 129.5, 143.5, 155.2, 156.6; **HRMS (ESI, m/z):** Calculated for $C_{17}H_{25}N_3O_4$ (M+H)+ 336.1923, found: 336.1923; **Analysis**: $C_{17}H_{25}N_3O_4$ requires: C, 60.88; H, 7.51; N, 12.53; found: C, 60.88; H, 7.51; N, 12.53%.

(R) - Diisopropyl 1 - (6,7-dimethoxy-1,2,3,4-tetrahydroquinolin-3-yl) hydrazine - 1,2 - dicarboxylate (6b)

Yield: 85% (1.68 g); gum, $[\alpha]^D_{25}$ -1379.0 (*c* 1.2, $CHCl_3$); 90% ee from **HPLC analysis**; Column: Chiracel OD-H (250 x 4.6 mm), mobile phase: isopropyl alcohol/n-hexane (5/95),

wavelength: 254 nm, flow rate: 0.5 mL/ min, conc.: 1.5 mg/mL, injection vol.: 10µL, retention time: 19.3 min (-)-isomer, 22.3 min (+)-isomer; **IR** ($CHCl_3$): 1036, 1108, 1133, 1179, 1385, 1398, 1519, 1707, 2999, 3313, 3378 cm^{-1}; **^{1}H NMR** (200 MHz, $CDCl_3$): δ 1.22-128 (m, 12H), 2.81-2.93 (m, 2H), 3.20-3.41 (m, 2H), 3.77 (s, 3H), 3.79 (s, 3H), 4.54-4.58 (m, 1H), 4.94-4.97 (m, 2H), 6.11 (s, 1H), 6.32 (br. s, 1H), 6.50 (s, 1H); **^{13}C NMR** (50 MHz, $CDCl_3$): δ 22.0, 29.6, 44.9, 51.6, 56.5, 69.2, 70.0, 96.1, 99.6, 111.2, 113.7, 137.5, 141.7, 148.3, 155.3, 156.7; **HRMS (ESI, m/z):** Calculated for $C_{19}H_{29}N_3O_6$ (M+H)+ 396.2135, found: 396.2131; **Analysis**: $C_{19}H_{29}N_3O_6$ requires: C, 57.71; H, 7.39; N, 10.63; found: C, 57.72; H, 7.33; N, 10.67%.

(R)-Diisopropyl 1-(5,6,7,8-tetrahydro-[1,3]dioxolo[4,5-g]quinolin-7-yl)hydrazine-1,2-dicarboxylate (6c)

Yield: 87% (1.65 g); gum, $[\alpha]^D_{25}$ -1694.1(*c* 0.7, $CHCl_3$); 91% ee from **HPLC analysis**; Column: Chiracel OD-H (250 x 4.6 mm), mobile phase: isopropyl alcohol/n-hexane (5/95), wavelength: 254 nm, flow rate: 0.5 mL/ min, conc.: 1.5mg/mL, injection vol.: 10µL, retention time: 20.3 min (-)-isomer, 27.9 min (+)-isomer; **IR** ($CHCl_3$): 1038, 1106, 1161, 1182, 1216, 1235, 1299, 1374, 1386, 1468, 1503, 1707, 2916, 2980, 3304 cm^{-1}; **^{1}H NMR** (200 MHz, $CDCl_3$): δ 1.23-1.28 (m, 12H), 2.82-2.98 (m, 2H), 3.13-3.42 (m, 2H), 4.51 (m, 1H), 4.94-4.97 (m, 2H), 5.30 (s, 1H), 5.80 (s, 2H), 6.09 (s, 1H), 6.28 (br. s, 1H), 6.44 (s, 1H); **^{13}C NMR** (50 MHz, $CDCl_3$): δ 21.9, 29.8, 44.7, 51.3, 69.4, 70.0, 96.6, 108.9, 111.6, 137.5, 139.9, 146.3, 155.0, 156.6; **Analysis**: $C_{18}H_{25}N_3O_6$ requires: C, 56.98; H, 6.64; N, 11.08; found: C, 56.52; H, 6.51; N, 11.18%.

(R)-Diisopropyl-1-(7-(cyclopentyloxy)-6-methoxy-1,2,3,4-tetrahydroquinolin-3-yl)hydrazine-1,2-dicarboxylate (6d)

Yield: 81% (1.82 g); gum, $[\alpha]^D_{25}$ -327.6 (*c* 3.4, $CHCl_3$); 91% ee from **HPLC analysis**; Column: Chiracel OD-H (250 x 4.6 mm), mobile phase: isopropyl alcohol/n-hexane (5/95), wavelength:

254 nm, flow rate: 0.5 mL/ min, conc.: 1.5 mg/mL, injection vol.: 10µL, retention time: 29.9 min (-)-isomer, 37.6 min (+)-isomer; **IR** ($CHCl_3$): 1035, 1108, 1135, 1198, 1227, 1253, 1299, 1340, 1374, 1385, 1397, 1515, 1712, 2978, 3296 cm^{-1}; **^{1}H NMR** (200 MHz, $CDCl_3$): δ 1.23-128 (m, 1H), 1.56-1.82 (m, 1H), 2.75-3.37 (m, 4H), 3.75 (s, 3H), 4.59 (m, 2H), 4.94-5.00 (m, 2H), 6.01 (s, 1H), 6.28 (br. s, 1H), 6.51 (s, 1H); **^{13}C NMR** (50 MHz, $CDCl_3$): δ 21.8, 22.0, 24.9, 29.6, 44.8, 51.2, 56.8, 69.4, 69.8, 80.1, 103.1, 111.1, 114.9, 137.4, 142.8, 146.8, 155.0, 156.5; **Analysis**: $C_{23}H_{35}N_3O_6$ requires: C, 61.45; H, 7.85; N, 9.35; found: C, 61.38; H, 7.84; N, 9.15%.

(*R*)- Diisopropyl 1-(7-(*tert*-butyldiphenylsilyloxy)-6-methoxy-1,2,3,4-tetrahydroquinolin-3-yl)hydrazine-1,2-dicarboxylate (6e)

Yield: 80% (2.46 g); gum, $[\alpha]^D_{25}$ -434.5 (*c* 3.2, $CHCl_3$); 90% ee from **HPLC analysis**; Column: Chiracel OD-H (250 x 4.6 mm), mobile phase: isopropyl alcohol/n-hexane (5/95), wavelength: 254 nm, flow rate: 0.5 mL/ min, conc.: 1.5mg/mL, injection vol.: 10µL, retention time: 35.5 min (-)-isomer, 41.99 min (+)-isomer; **IR** ($CHCl_3$): 702, 1109, 1143, 1228, 1255, 1298, 1385, 1518, 1710, 2856, 2931, 2979, 3283 cm^{-1}; **^{1}H NMR** (200 MHz, $CDCl_3$): δ 1.25 (t, *J* = 4.5, 12.8 Hz, 1H), 2.93 (m, 1H), 3.20-3.40 (m, 2H), 3.77 (s, 3H), 3.79 (s, 3H), 4.55 (m, 1H), 4.94 (m, 2H), 6.11 (s, 1H), 6.32 (brs, 1H), 6.50 (s, 1H); **^{13}C NMR** (50 MHz, $CDCl_3$): δ 19.7, 21.9, 26.6, 29.5, 51.2, 56.5, 69.4, 69.7, 107.1, 115.1, 127.4, 129.4, 133.6, 135.2, 137.2, 143.2, 144.3; **Analysis**: $C_{34}H_{45}N_3O_6Si$ requires: C, 65.88; H, 7.32; N, 6.78; found: C, 65.80; H, 7.02; N, 6.56 %.

2-(2-Nitrophenyl)ethanol (8)

To a stirred solution of ester **7** (7.0 g, 31.7 mmol), $CoCl_2{\cdot}6H_2O$ (377 mg, 5 mol %) and diisopropyl amine (320 mg, 10 mol %) in 95% ethanol (100 mL) was added $NaBH_4$ (4.8 g, 126.8 mmol) slowly at 25 °C. It was then stirred for 24 h at 50-60 °C. After completion of the reaction (monitored by TLC), it was quenched with addition of water (20 mL) and ethyl acetate (100

mL). The organic layer was separated and the aqueous layer extracted with ethyl acetate (2 x 50 mL). The combined organic layers were washed with brine (2 x 20 mL), dried over anhydrous Na_2SO_4 and concentrated under reduced pressure to give the crude product. Chromatographic purification of crude product with pet. ether/ethyl acetate (7:3 v/v) afforded alcohol **8** as gum.

Yield: 85% (5.74 g); **IR** ($CHCl_3$): υ_{max} 857, 968, 1029, 1060, 1245, 1440, 1507, 3430 cm^{-1}; **^{1}H NMR** (200 MHz, $CDCl_3$): δ 1.85-1.99 (m, 2H), 2.14 (br s, 1H), 2.98 (t, *J* = 7.6 Hz, 2H), 3.70 (t, *J* = 6.2 Hz, 2H), 7.31-7.55 (m, 3H), 7.86 (d, *J* = 7.7 Hz, 1H); **^{13}C NMR** (50 MHz, $CDCl_3$): δ 29.1, 33.2, 61.6, 124.4, 126.8, 131.8, 132.8, 136.7, 149.1; **Anal.** Calcd for $C_9H_{11}NO_3$ requires C, 59.66; H, 6.12; N, 7.73; found: C, 59.71; H, 6.15; N, 7.79%.

3-(2-Nitrophenyl)propanal (4a)

To a stirred solution of alcohol **8** (5 g, 27.60 mmol) in dry CH_2Cl_2 (100 mL), PCC (11.9 g, 55.20 mmol) was added slowly at 25 °C. It was then stirred for additional 6 h. After completion of the reaction (monitored by TLC), it was passed through a short pad of silica gel (230-400 mesh) using CH_2Cl_2 as eluent. The combined organic layers were concentrated under reduced pressure to give aldehyde **4a** which was pure enough to be used for the next step.

Yield: 85% (4.2 g); gum; **IR** ($CHCl_3$): υ_{max} 667, 756, 850, 1155, 1215, 1253, 1278, 1345, 1476, 1712, 2989, 3123 cm^{-1}; **^{1}H NMR** (200 MHz, $CDCl_3$): δ 2.89 (t, *J* = 7.3 Hz, 2H), 3.20 (t, *J* = 7.3 Hz, 2H), 7.34-7.58 (m, 3H), 7.92 (d, *J* = 7.9 Hz, 2H), 9.82 (s, 1H); **^{13}C NMR** (50 MHz, $CDCl_3$): δ 25.6, 44.4, 124.9, 127.5, 132.3, 133.1, 135.7, 199.9; **Anal.** Calcd for $C_9H_9NO_3$ requires: C, 60.33; H, 5.06; N, 7.82; found: C, 60.38; H, 5.11; N, 7.76%.

(*S*)-1,2,3,4-Tetrahydroquinolin-3-ol (9)

Yield: 71% (633 mg); gum, $[\alpha]^D_{25}$ –20.9 (*c* 1, $CHCl_3$); 96% ee (HPLC).

(*S*)-Methyl 3-hydroxy-3,4-dihydroquinoline-1(2H)-carboxylate (10)

To a stirred solution of tetrahydroquinolin-3-ol **9** (200 mg, 1.34 mmol) and methyl chloroformate (1 mL, 13 mmol) in CH_2Cl_2/H_2O (4:1), was added K_2CO_3 (1.8 g, 13 mmol) at 0 ºC and the reaction mixture was further allowed to stir for 6 h at 25 ºC. Progress of reaction was monitored by TLC and after completion of reaction, a saturated solution of NH_4Cl (20 mL) was added. The organic layer was separated; the aqueous layer extracted with CH_2Cl_2 (2 x 50 mL). Combined organic layers were washed with brine (2 x 25 mL), dried over anhydrous Na_2SO_4 and concentrated under reduced pressure to give the crude products. Chromatographic purification of crude product with pet. ether/ethyl acetate (6: 4 v/v) as eluent gave **10** as oily liquid.

Yield: 98% (291 mg); $[\alpha]^D_{25}$ +21.9 (*c* 1, $CHCl_3$); **IR** ($CHCl_3$): υ_{max} 1469, 1589, 1608, 1704, 3419 cm^{-1}; **^{1}H NMR** (200 MHz, $CDCl_3$): δ 2.71-2.82 (m, 2H), 3.00 (dd, *J* = 5.3, 16.7 Hz, 1 H), 3.70-3.84 (m, 5H), 4.21 (m, 1H), 7.01-7.19 (m, 3H), 7.58 (d, *J* = 8.1 Hz, 1 H); **^{13}C NMR** (50 MHz, $CDCl_3$): δ 35.9, 50.4, 53.0, 64.7, 123.8, 124.3, 126.1, 126.8, 129.4, 137.4, 155.7; **ESIMS** (m/z) 208 $[M+H]^+$; **HRMS** (ESI): calcd. for $C_{11}H_{13}NO_3$ 208.0974; found: 208.0969.

(*R*)-Methyl 3-azido-3,4-dihydroquinoline-1(2H)-carboxylate (11)

To a stirred solution of alcohol **10** (170 mg, 0.84 mmol) in anhydrous CH_2Cl_2 (16 mL) kept at 0 °C under nitrogen were successively added freshly distilled Et_3N (0.4 mL, 2.5 mmol) and mesyl chloride (0.1 mL, 1.26 mmol). After stirring was continued for 45 min, CH_2Cl_2 (90 mL) was added to the reaction mixture, which was then washed sequentially with saturated aqueous sodium hydrogen carbonate and brine, dried with anhydrous Na_2SO_4, and concentrated under reduced pressure. To a solution of this crude mesylate in anhydrous DMF (10 mL) kept at 80 °C under nitrogen was added sodium azide (0.199 g, 3.1 mmol). The resulting solution was stirred at 80 °C for 4 h. Progress of the reaction was monitored by TLC and after completion of reaction, it was extracted with EtOAc. The combined organic layers were dried over anhydrous Na_2SO_4 and

then concentrated in vacuo. The crude product was purified by column chromatography with pet. ether/EtOAc (9:1 v/v) to give azide **11** as yellow liquid.

Yield: 93% (181 mg); $[\alpha]^{D}_{25}$ -28.2 (*c* 1, $CHCl_3$); **IR** ($CHCl_3$): υ_{max} 1493, 1708, 2104, 2953 cm^{-1}; **^{1}H NMR** (200 MHz, $CDCl_3$): δ 2.80 (dd, *J* = 6.2, 16.4 Hz, 1 H), 3.08 (dd, *J* = 6.3, 17.0 Hz, 1 H), 3.68-3.82 (m, 4H), 3.92-4.03 (m, 2H), 7.04-7.20 (m, 3H), 7.62 (d, *J* = 8.1 Hz, 1 H); **^{13}C NMR** (50 MHz, $CDCl_3$): δ 32.8, 47.6, 53.2, 55.3, 123.9, 124.4, 125.6, 126.7, 129.0, 137.4, 155.0; **ESIMS** (m/z) 255 $[M+Na]^+$; **HRMS** (ESI): calcd. for $C_{11}H_{12}N_4O_2$ 255.0858; found: 255.0889.

(*R*)-Methyl 3-azido-6-bromo-3,4-dihydroquinoline-1(2H)-carboxylate (12)

To a stirred solution of azide **11** (120 mg, 0.52 mmol) in acetic acid were successively added anhydrous NaOAc (212 mg, 1.9 mmol) and Br_2 (0.3 mL, 0.52 mmol). The mixture was stirred at 25 °C for 1 h and then quenched with water (30 mL). The resulting solution was extracted with CH_2Cl_2 (2 x 30 mL). The combined organic layers were dried with anhydrous Na_2SO_4 and concentrated in vacuo. The residue was purified over column chromatography with pet. ether/EtOAc (9:1 v/v) to give bromo azide **12** as thick liquid.

Yield: 95% (153 mg); $[\alpha]^{D}_{25}$ -14.2 (*c* 1, $CHCl_3$); **IR** ($CHCl_3$): υ_{max} 910, 1264, 1458, 1716, 2103 cm^{-1}; **^{1}H NMR** (200 MHz, $CDCl_3$): δ 2.78 (dd, *J* = 5.9, 16.8 Hz, 1H), 3.08 (dd, *J* = 5.7, 16.8 Hz, 1H), 3.77-3.96 (m, 5H), 4.01-4.04 (m, 1H), 7.25-7.33 (m, 2H), 7.55 (d, *J* = 8.7 Hz, 1H); **^{13}C NMR** (50 MHz, $CDCl_3$): δ 35.7, 50.3, 53.3, 64.4, 117.0, 130.0, 124.5, 125.7, 128.9, 129.6, 132.3, 136.4, 155.1; **ESIMS** (m/z) 332 $[M+Na]^+$; **HRMS** (ESI): calcd. for $C_{11}H_{11}BrN_4O_2$ 332.9963; found: 332.9998.

(*R*)-Methyl 3-azido-6-bromo-8-nitro-3,4-dihydroquinoline-1(2H)-carboxylate (13)

To a solution of sodium nitrate (30 mg, 0.35 mmol) in trifluoroacetic acid (5 mL) was added bromo azide **12** (100 mg, 0.32 mmol). The resulting solution was stirred at 25 °C for 30 min and

then concentrated under reduced pressure. The crude product was then dissolved in EtOAc (50 mL) and the organic portion washed sequentially with saturated aqueous sodium hydrogen carbonate (10 mL), NaOH (1 M solution, 10 mL), and water (10 mL), dried with anhydrous Na_2SO_4, and then concentrated under reduced pressure. It was purified by column chromatography with pet. ether/EtOAc (6:4 v/v) to give nitro compound **13** as a thick liquid.

Yield: 95% (108 mg); $[\alpha]^D_{25}$ +59.3 (*c* 1, $CHCl_3$) {lit.[17] $[\alpha]^D_{25}$ +58.4 (*c* 0.51, $CHCl_3$)}; **IR** ($CHCl_3$): υ_{max} 1265, 1456, 1717, 2105 cm^{-1}; **^{1}H NMR** (200 MHz, $CDCl_3$): δ 2.86 (dd, *J* = 5.4, 16.8 Hz, 1H), 3.08 (dd, *J* = 5.1, 16.7 Hz, 1H), 3.64-3.80 (m, 5H), 4.09-4.16 (m, 1H), 7.51 (s, 1H); 7.91 (d, *J* = 2.1 Hz, 1H); **^{13}C NMR** (50 MHz, $CDCl_3$): δ 32.7, 47.5, 53.2, 55.5, 117.4, 123.0, 126.5, 134.8, 135.8, 144.3, 153.4; **ESIMS** (m/z) 393 $[M+K]^+$; **HRMS** (ESI): calcd. for $C_{11}H_{10}BrN_5O_4$ 393.9553; found 393.9513.

(*S*)-Di-*tert*-butyl-1-(6,7-dimethoxy-1,2,3,4-tetrahydroquinolin-3-yl)hydrazine-1,2-dicarboxylate (14)

To a stirred solution of nitro hydrocinnamaldehyde **4b** (1.31 g, 5.5 mmol) and di-*tert*-butyl azodicarboxylate (1.15 g, 5.0 mmol) in CH_3CN (10 mL), was added D-proline (20 mol %) at 0 ºC and allowed to stir for 3 h. After the completion of reaction as indicated by the disappearance of yellow color, was added MeOH (30 mL) and 10% Pd/C (5 wt%). The reaction mixture was then stirred at 25 ^oC for additional 6 h under H_2 atmosphere (1atm, balloon pressure). After the completion of reaction (monitored by TLC), it was filtered through a pad of celite and the solvent evaporated under reduced pressure. Chromatographic purification of the crude product [flash silica gel (230-400 mesh) and pet. ether:EtOAc (70:30)] gave the pure **14**.

Yield: 83% (1.76 g); gum, $[\alpha]^D_{25}$ +409.1 (*c* 1.5, $CHCl_3$); **IR** ($CHCl_3$): 1158, 1207, 1252, 1366, 1391, 1518, 1704, 2929, 2977, 3323 cm^{-1}; ^{1}H **NMR** (200 MHz, $CDCl_3$): 1.44-1.48 (m, 18H), 1.80 (brs, 1H), 2.85-3.01 (m, 2H), 3.09-3.46 (m, 2H), 3.78 (s, 3H), 3.7 (s, 3H), 4.44-4.54 (m,

1H), 6.1 (s, 1H), 6.16 (brs, 1H), 6.50 (s, 1H); **^{13}C NMR** (50 MHz, $CDCl_3$): δ 28.0, 29.4 ,44.8, 50.7, 55.5, 56.4, 77.0, 80.6, 81.0, 95.9, 99.6, 111.3, 113.7, 137.3, 141.6, 148.0, 154.5, 155.8; **Analysis** for $C_{21}H_{33}N_3O_6$ requires C, 59.56; H, 7.85; N, 9.92; found: C, 59.52; H, 7.81; N, 9.88%.

Synthesis of (S)-di-*tert*-butyl-1-(6,7-dimethoxy-1-Propionyl-1,2,3,4-tetrahydroquinolin-3-yl)hydrazine-1,2-dicarboxylate (15)

To the stirred solution of tetrahydroquinolin-3-hydrazine *tert*-butyl ester **14** (1.5 g, 3.6 mmol) and Et_3N (0.722 g, 7.2 mmol) in 25 mL of CH_2Cl_2, was added propionic anhydride (0.930 g, 7.2mmol) at 25 ^oC. Reaction mixture was then stirred for 3 h and after completion of reaction (monitored by TLC), it was washed sequentially with saturated aq. $NaHCO_3$ and brine, dried with anhydrous Na_2SO_4, and concentrated under reduced pressure to give crude product. Chromatographic purification of crude product [silica gel (230-400 mesh) and pet. ether:EtOAc (60:40)] gave amide **15** in pure form.

Yield 91% (1.56 g): gum, , $[\alpha]^D_{25}$ -382.6 (*c* 2.0, $CHCl_3$); **IR** ($CHCl_3$): 758, 1044, 1172, 1275, 1367, 1393, 1643, 1706, 1737, 2934, 2977, 3328 cm^{-1}: **^{1}H NMR** (200 MHz, $CDCl_3$): 1.12-1.23 (m, 3H), 1.45-1.48 (m, 18H), 1.65-1.71 (m, 2H), 2.43-2.58 (m, 2H), 2.84-3.00 (m, 2H), 3.85 (s, 6H), 4.43-4.59 (m, 1H), 6.22 (s, 1H), 6.63 (s, 1H); **^{13}C NMR** (50 MHz, $CDCl_3$): δ 8.9, 9.7, 27.0, 27.6, 28.1, 29.8, 55.8, 81.4, 108.4, 111.2, 154.4; **Analysis** for $C_{24}H_{37}N_3O_7$ requires C, 60.11; H, 7.78; N, 8.76; found C, 60.08; H, 7.74; N, 8.72%.

(S)-1-(3-Hydrazinyl-6,7-dimethoxy-3,4-dihydroquinolin-1(2H)-yl)propan-1-one (16)

To a ice-cooled solution of **15** (1.40 g, 2.9 mmol) in dry CH_2Cl_2 (15 mL) was added trifluoro acetic acid (2.0 g, 17.5 mmol). The reaction mixture was stirred at room temperature for 12 h. After the completion of the reaction (monitored by TLC) it was then quenched with saturated

aqueous $NaHCO_3$ and extracted with CH_2Cl_2 (3×5 mL). The combined organic layers were washed with brine and dried over anhyd. Na_2SO_4 and concentrated under reduced pressure to give the crude product. Chromatographic purification [silica gel (230-400 mesh) of the crude product using MeOH:EtOAc (5:95)] gave pure hydrazine **16** as colorless solid.

Yield 90% (0.736 g): solid, **mp** 104-108 °C; $[\alpha]^{D}_{25}$ +18.3 (*c* 1.1, MeOH); **IR** ($CHCl_3$): 749, 838, 1144, 1207, 1229, 1254, 1523, 1643, 2931, 2990, 3184, 3283 cm^{-1}; **^{1}H NMR** (200 MHz,$CDCl_3$): 1.17 (t, *J* = 7.6 Hz, 3H), 2.17 (q, *J* = 7.4, 15.0 Hz, 2H), 2.57 (dd, *J* = 4.3, 15.5 Hz, 2H), 2.89 (dd, *J* = 4.3, 16.3 Hz, 1H), 3.23-3.40 (m, 5H), 3.78 (s, 6H), 6.20 (s, 1H), 6.50 (s, 1H), 7.54 (brs, 1H**);** **^{13}C NMR** (50 MHz, $CDCl_3$): δ 9.6, 14.2, 27.7, 29.7, 42.9, 49.4, 56.3, 106.3, 111.8, 119.7, 122.0, 148.3, 149.6, 174.7; **HRMS (ESI, m/z):** Calculated for $C_{14}H_{21}N_3O_3$ (M+H)+ 280.1661, found: 280.1664; **Analysis** for $C_{14}H_{21}N_3O_3$ requires C, 60.20; H, 7.58; N, 15.04; found: C, 60.15; H, 7.52; N, 15%.

1-[(*R*)-3-(Dimethylamino)-3,4-dihydro-6,7-dimethoxyquinolin-1(2*H*)-yl]-propan-1-one (2)

A solution of hydrazine **16** (560 mg, 2 mmol) in MeOH (10 mL), and AcOH (10 drops) was treated with Raney nickel (2 g, excess) under H_2 (80 psig) atmosphere for 24 h. After the completion of reaction (monitored by TLC), it was passed through a column packed with celite and concentrated under reduced pressure to afford the crude amine. To the crude amine, 40% aq. solution of HCHO (1 mL) and HCO_2H (2 mL) were added and the resulting mixture was refluxed for 3 h. After completion of the reaction, a saturated aq. $NaHCO_3$ solution (10 mL) was added and the mixture extracted with EtOAc (3 x 20 mL). The combined organic layer was washed with brine (2 x 20 mL), dried over anhyd. Na_2SO_4, concentrated under reduced pressure. Chromatographic purification of the crude product [silica gel (230-400 mesh) and pet. ether: ethyl acetate: Et_3N (60:38:2) as eluent] gave pure **(*S*)-903** (**2**).

Yield: 73% (0.425 mg); **mp** 136 °C [lit.[18] 135-137 °C]; $[\alpha]^{D}_{25}$ –3.2 (*c* 1, EtOH) {lit.[18] $[\alpha]^{D}_{25}$ – 3.3 (*c* 1, EtOH)}; **IR** ($CHCl_3$): 760, 1049, 1211, 1511, 1647, 1743, 3018, 3450 cm^{-1}; **^{1}H NMR** (200 MHz, $CDCl_3$): δ 1.12 (t, *J* = 7.3 Hz, 3H), 2.35 (s, 6H), 2.46 (q, *J* = 7.3 Hz, 2H), 2.80-2.91 (m, 2H), 3.23-3.54 (m, 2H), 3.82 (s, 3H), 3.83 (s, 3H), 6.64 (bs, 2H); **^{13}C NMR** (50 MHz, $CDCl_3$): δ 9.8, 27.5, 29.5, 41.3, 41.4, 55.9, 55.9, 61.4, 61.8, 108.2, 111.1, 128.6, 131.8, 146.9, 173.0; **Analysis** for $C_{15}H_{21}N_2O_3$ requires C, 64.96; H, 7.63; N, 10.10; found: C, 64.82; H, 7.60; N, 10.27%.

3. Spectral Data

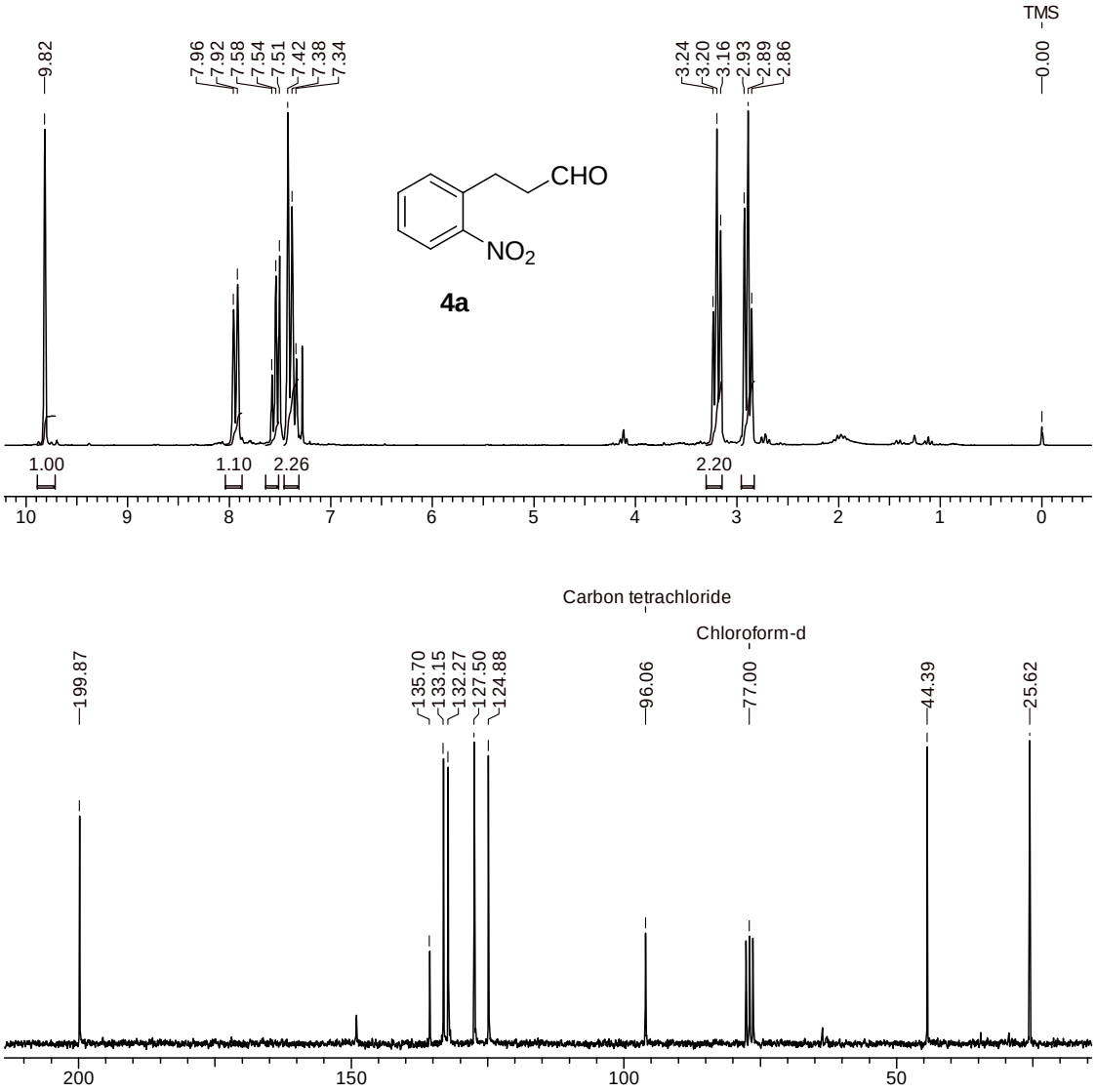


Figure 1: ^{1}H and ^{13}C NMR spectra of *o*-nitrohydrocinnamaldehyde **4a**

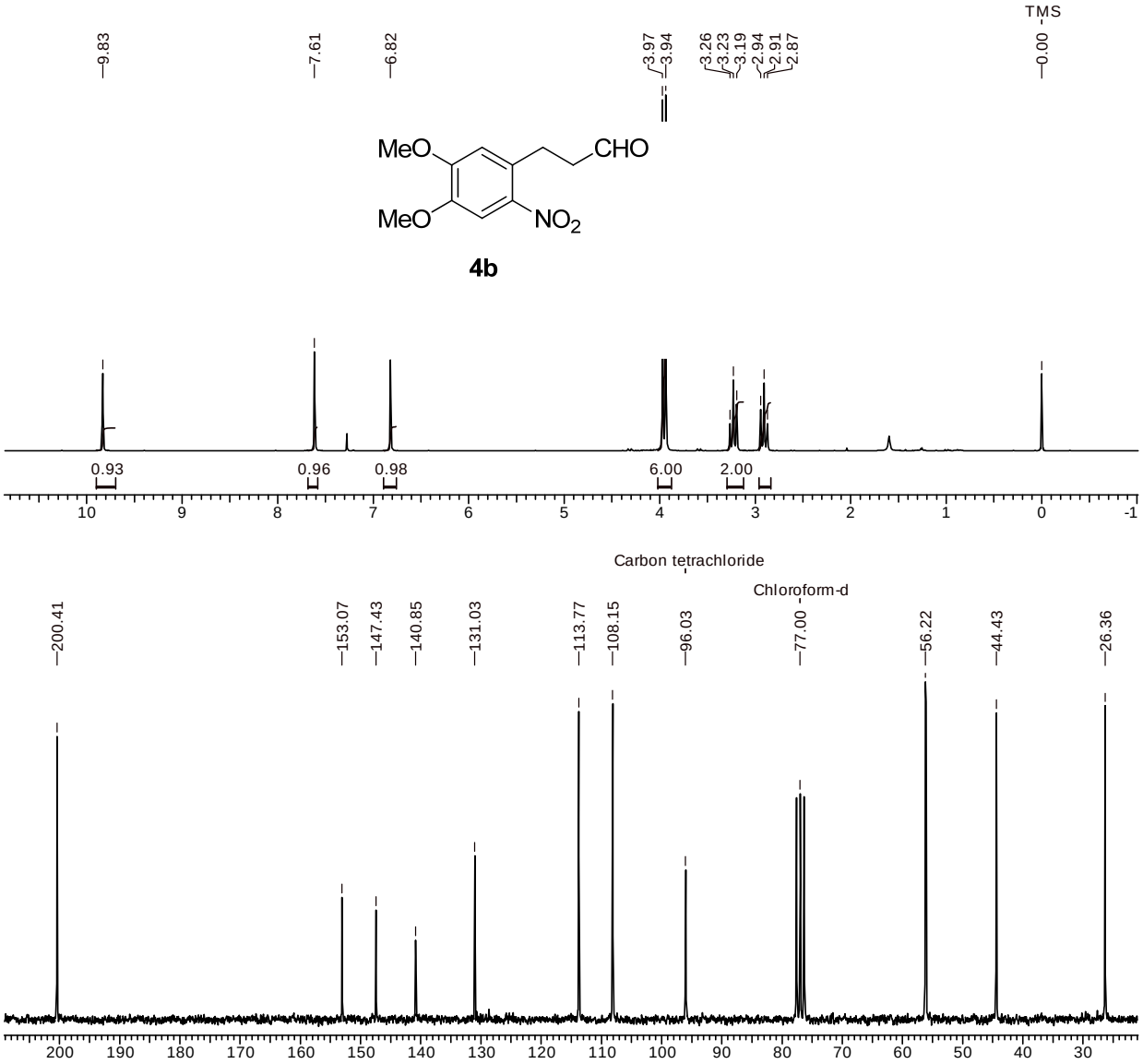


Figure 2: ^{1}H and ^{13}C NMR spectra of dimethoxy nitro aldehyde **4b**

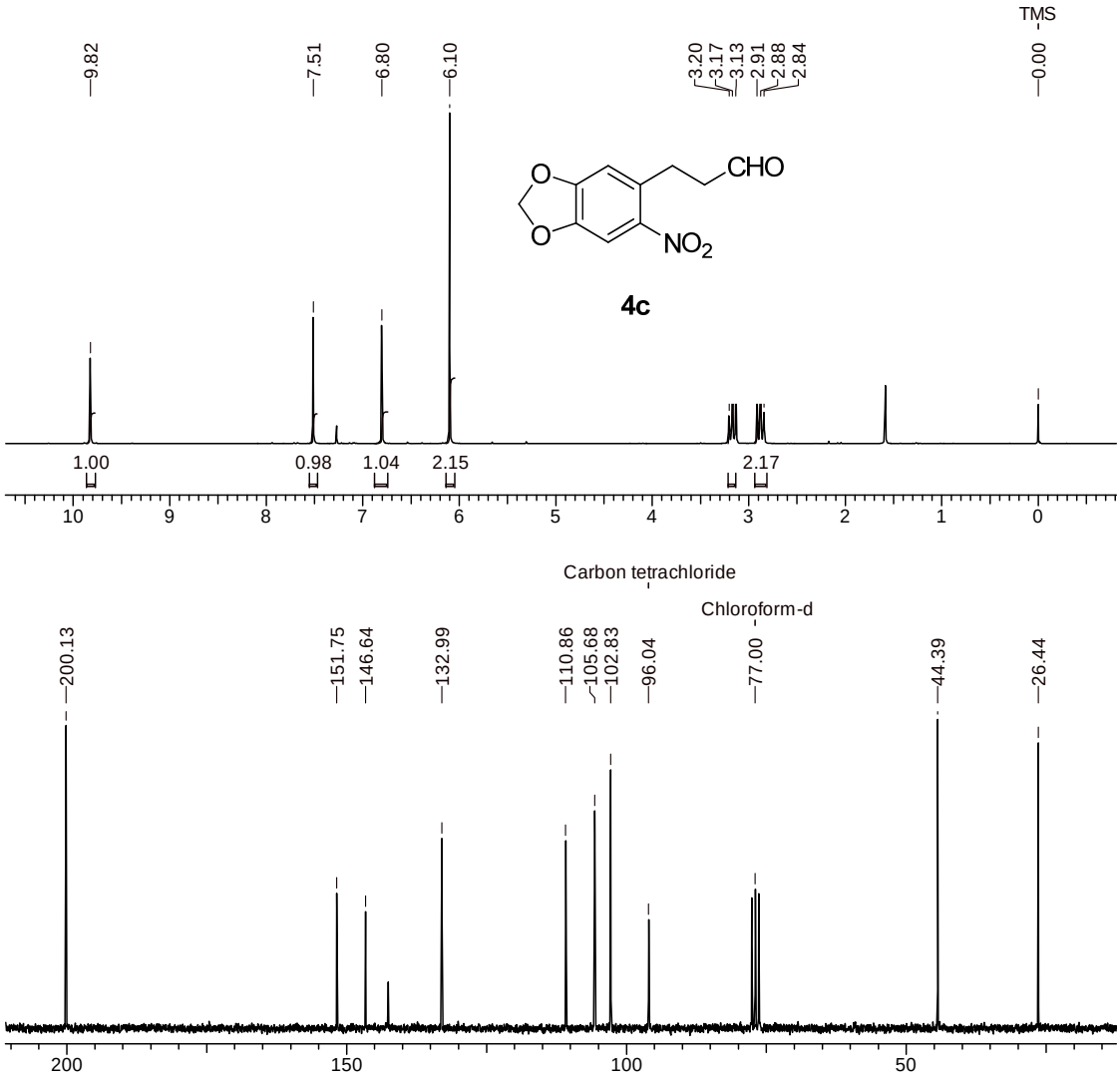


Figure 3: ^{1}H and ^{13}C NMR spectra of *o*-nitrohydrocinnamaldehyde **4c**

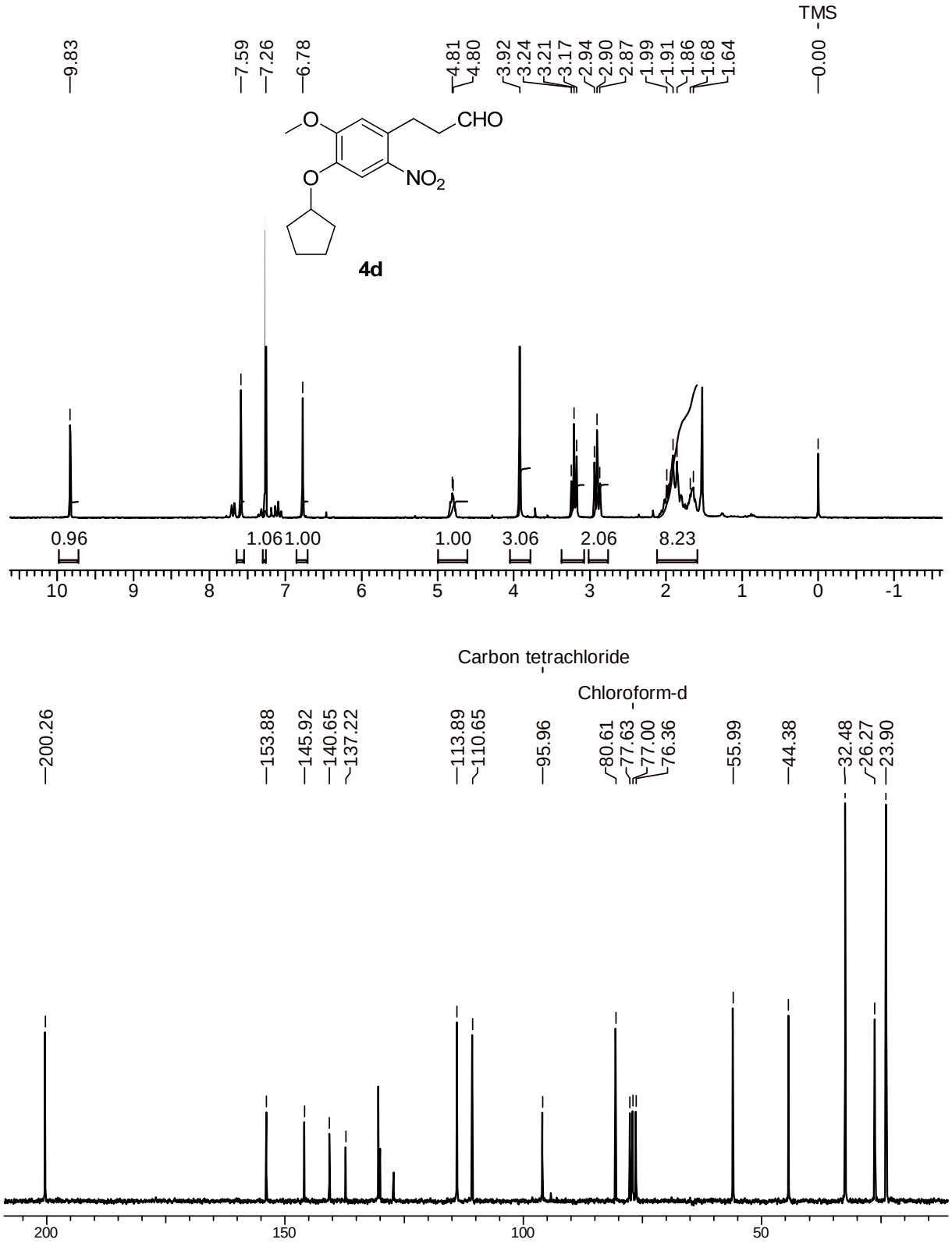


Figure 3: ^{1}H and ^{13}C NMR spectra of *o*-nitrohydrocinnamaldehyde **4d**

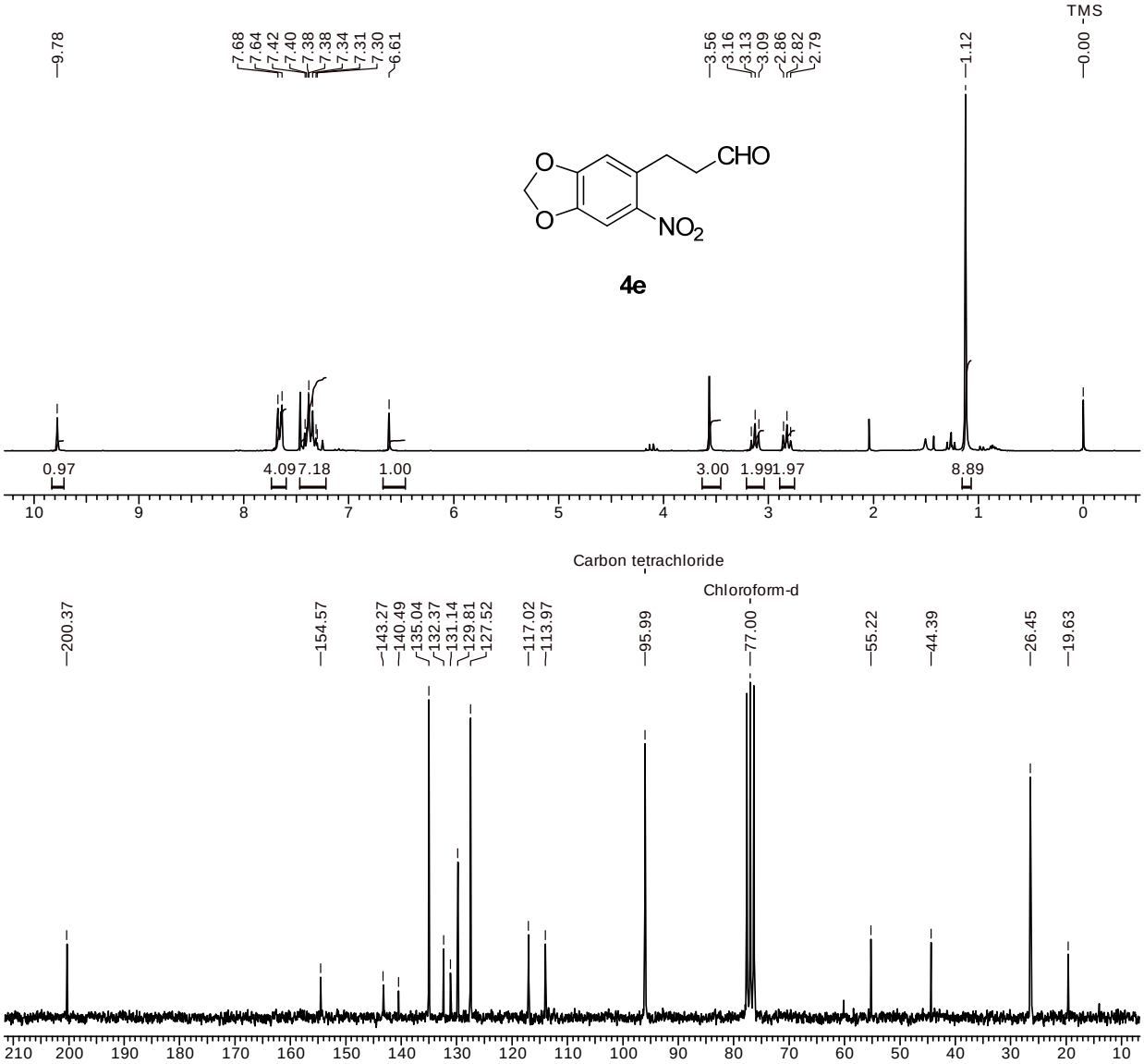
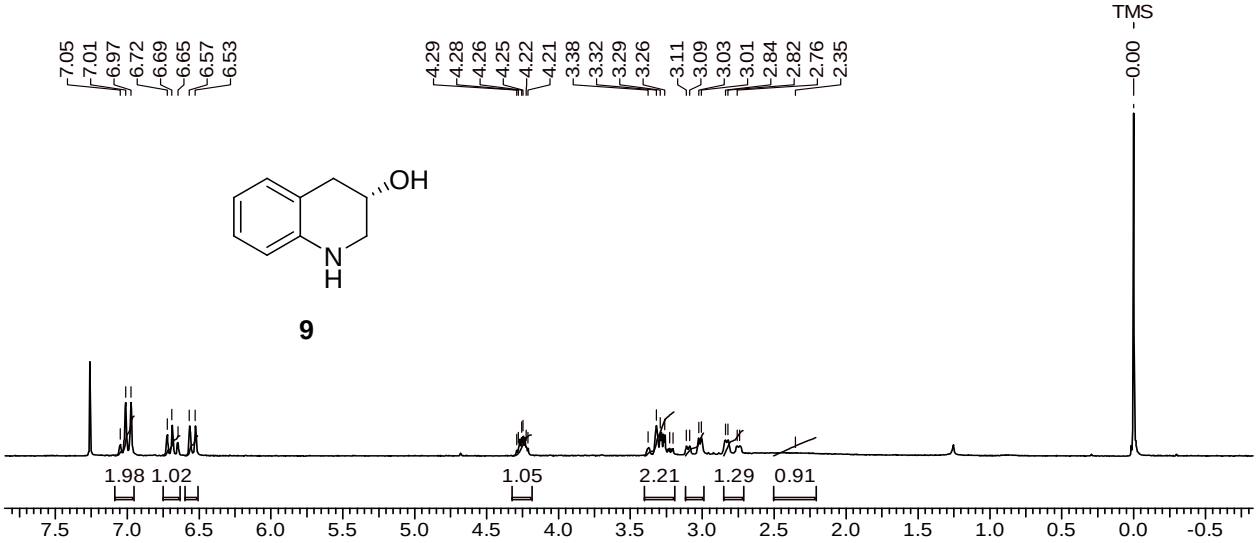


Figure 5: ^{1}H and ^{13}C of OTBDPS nitro aldehyde **4e**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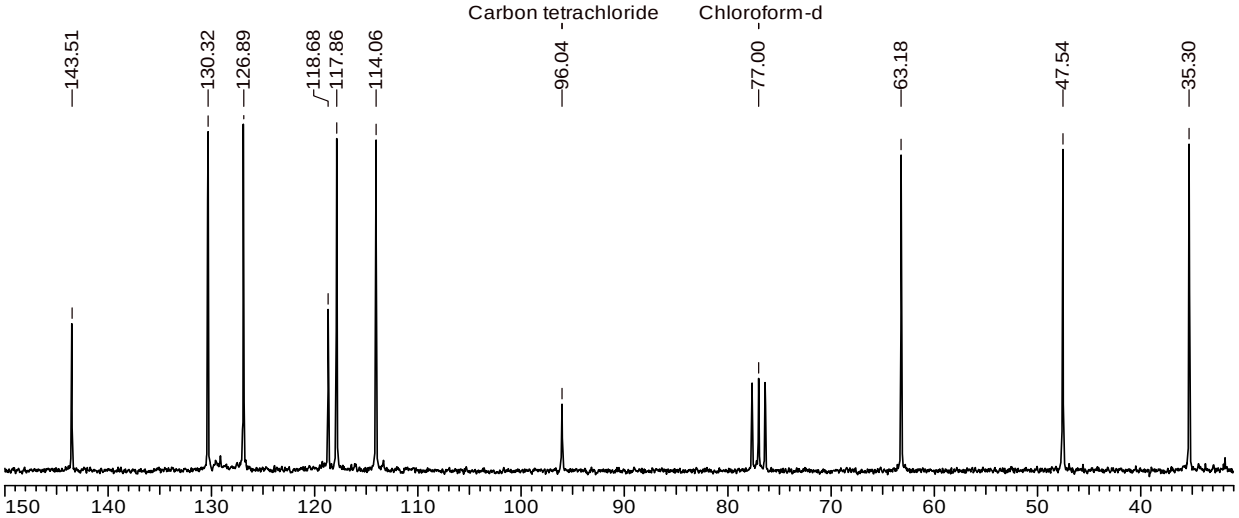
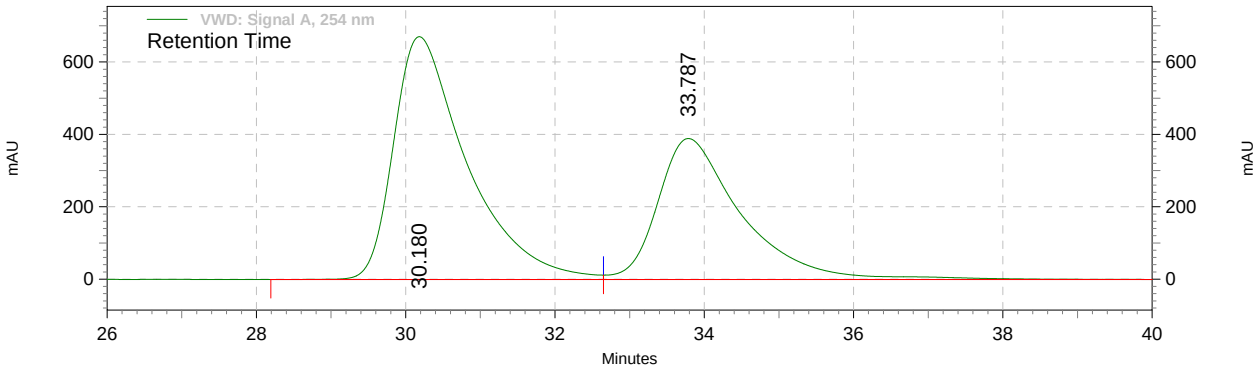
7.05
7.01
6.97
6.72
6.69
6.65
6.57
6.53
4.29
4.28
4.26
4.25
4.22
4.21
3.38
3.32
3.29
3.26
3.11
3.09
3.03
3.01
2.84
2.82
2.76
2.35
0.00
OH
N
H
9
1.98 1.02
1.05
2.21
1.29
0.91
7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5


Carbon tetrachloride
Chloroform-d
143.51
130.32
126.89
118.68
117.86
114.06
96.04
77.00
63.18
47.54
35.30
150 140 130 120 110 100 90 80 70 60 50 40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mAU
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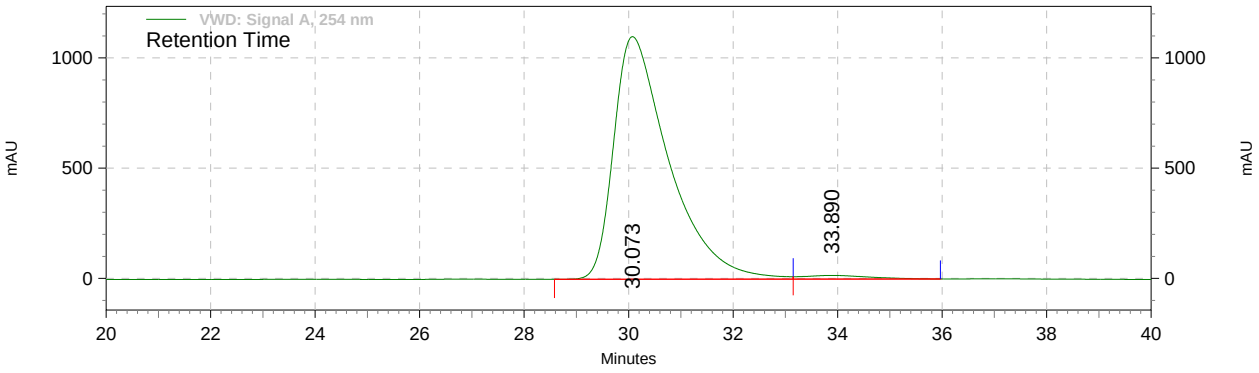
400
200
0
30.180
33.787
26 28 30 32 34 36 38 40
Minutes



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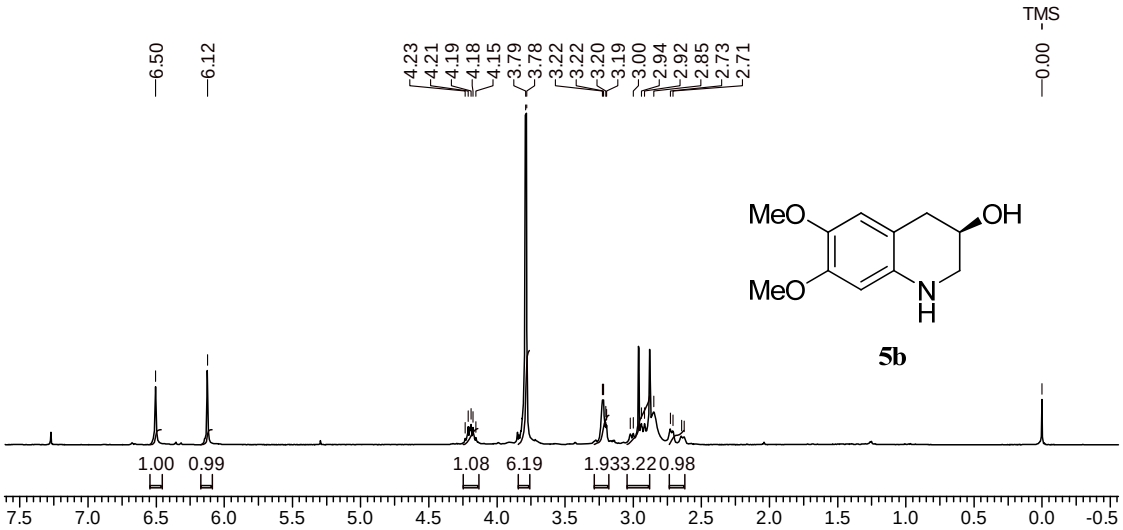
33.890	24389470	1.77	278235	1.48
Totals	1379938884	100.00	18744842	100.00

Figure 6: ^{1}H & ^{13}C NMR spectrum and chiral HPLC chromatogram of THQ **9**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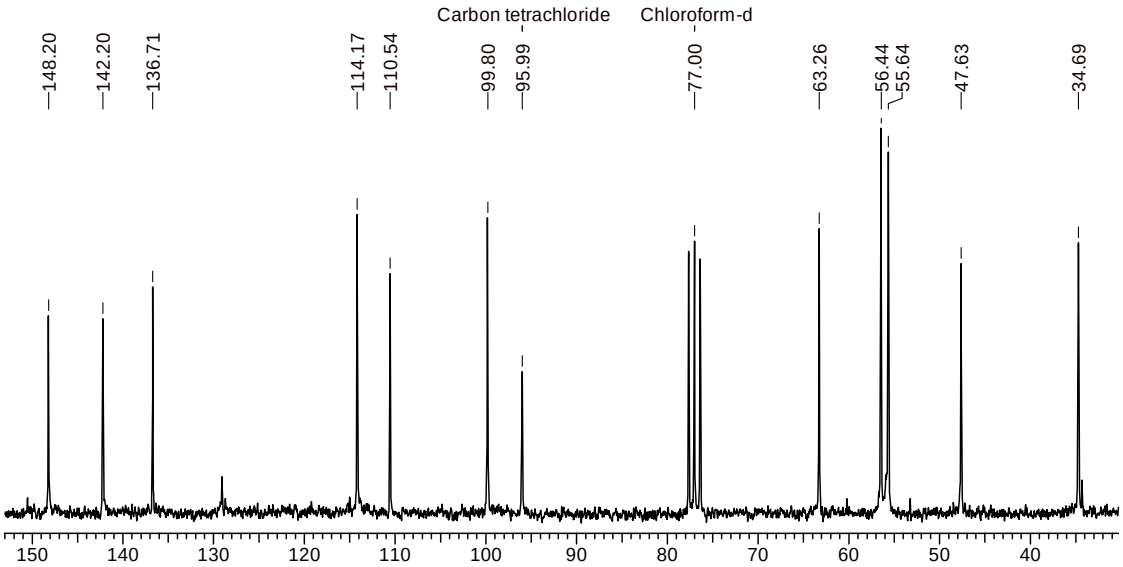
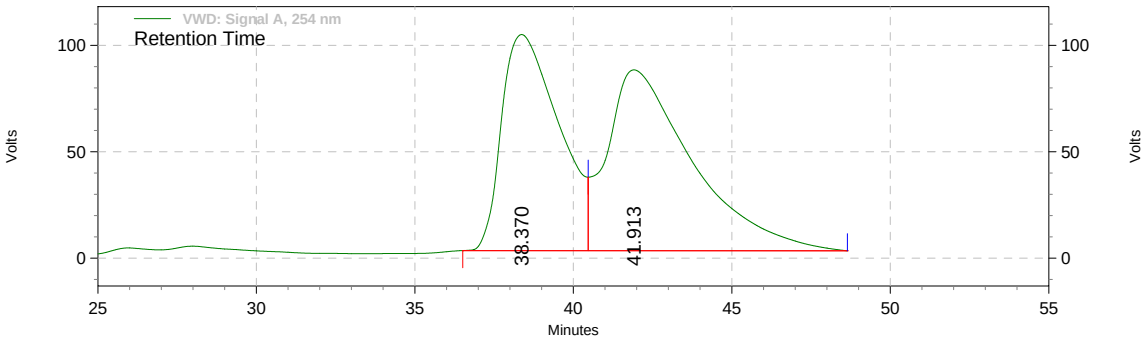
6.12
4.23
4.21
4.19
4.18
4.15
3.79
3.78
3.22
3.22
3.20
3.19
3.00
2.94
2.92
2.85
2.73
2.71
0.00
MeO
MeO
OH
N
H
5b
1.00
0.99
1.08
6.19
1.93
3.22
0.98
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5


Carbon tetrachloride
Chloroform-d
148.20
142.20
136.71
114.17
110.54
99.80
95.99
77.00
63.26
56.44
55.64
47.63
34.69
150
140
130
120
110
100
90
80
70
60
50
40


VWD: Signal A, 254 nm
Retention Time
Volts
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50
0
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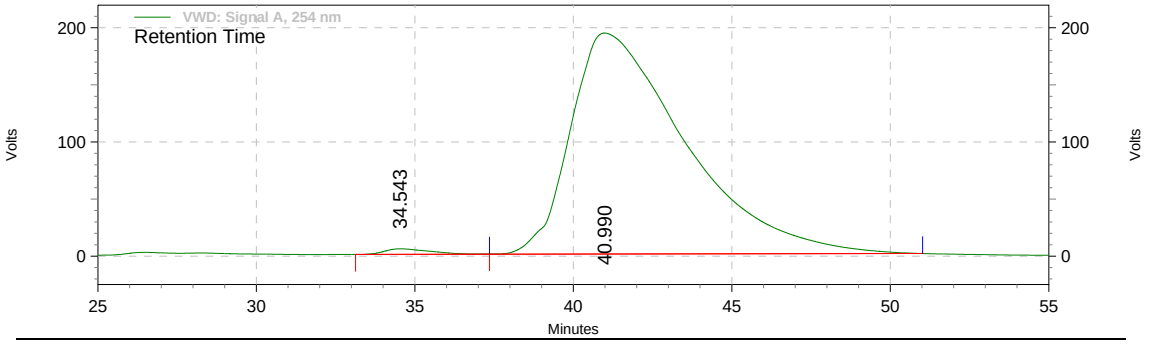
41.913
25
30
35
40
45
50
55
Minutes



Retention Time	Area	Area %	Height	Height %
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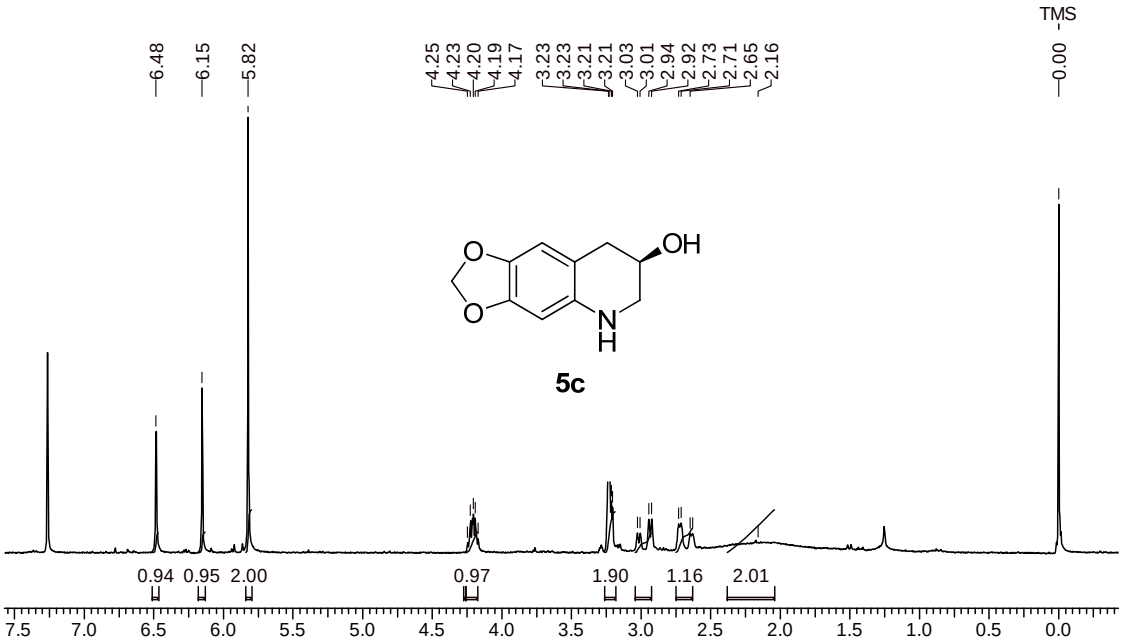
40.990	816959267	99.00	3246502	97.52
Totals	825246439	100.00	3329151	100.00

Figure 7: ^{1}H & ^{13}C NMR spectra and HPLC chromatogram of THQ **5b**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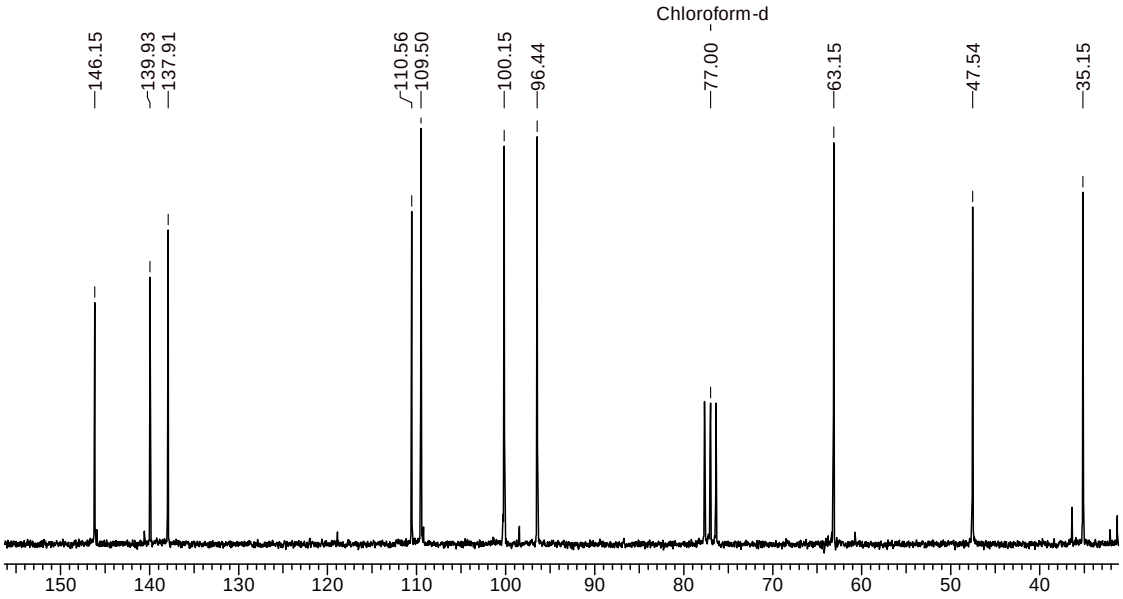
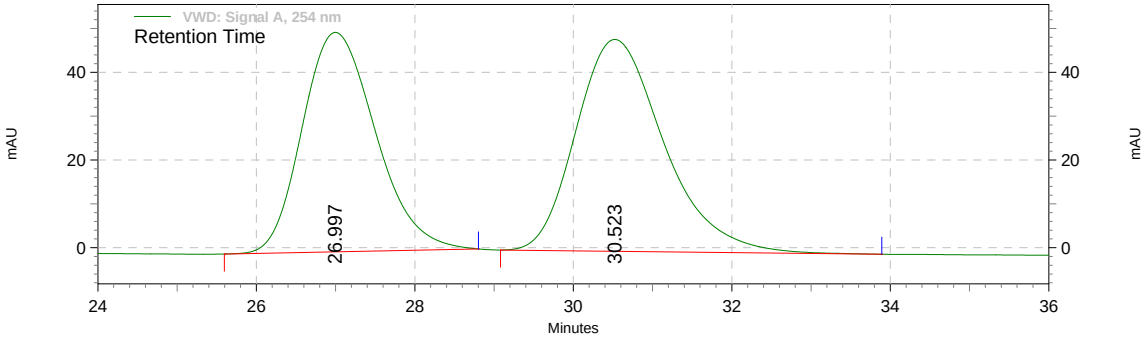
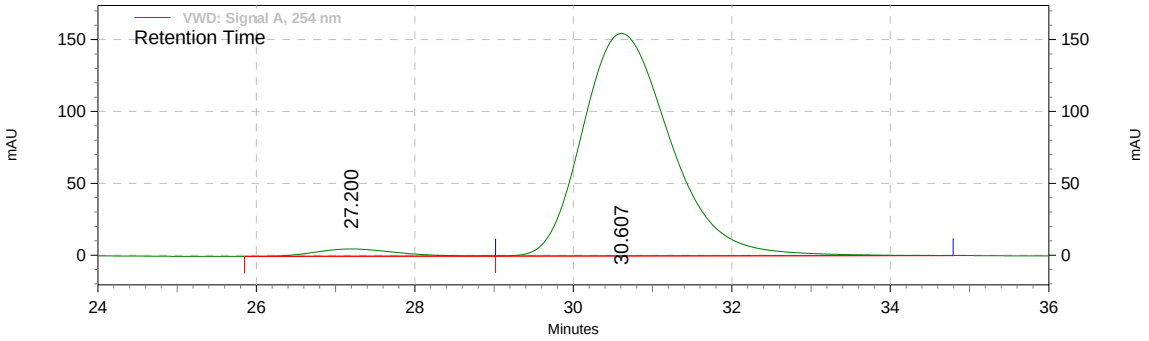
4.25
4.23
4.20
4.19
4.17
3.23
3.23
3.21
3.21
3.03
3.01
2.94
2.92
2.73
2.71
2.65
2.16
0.00
OH
O
O
N
H
5c
0.94 0.95 2.00
0.97
1.90
1.16
2.01
7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0


Chloroform-d
146.15
139.93
137.91
110.56
109.50
100.15
96.44
77.00
63.15
47.54
35.15
150 140 130 120 110 100 90 80 70 60 50 40


VWD: Signal A, 254 nm
Retention Time
mAU
40
20
0
26.997
30.523
24 26 28 30 32 34 36
Minutes



Retention Time	Area	Area %	Height	Height %
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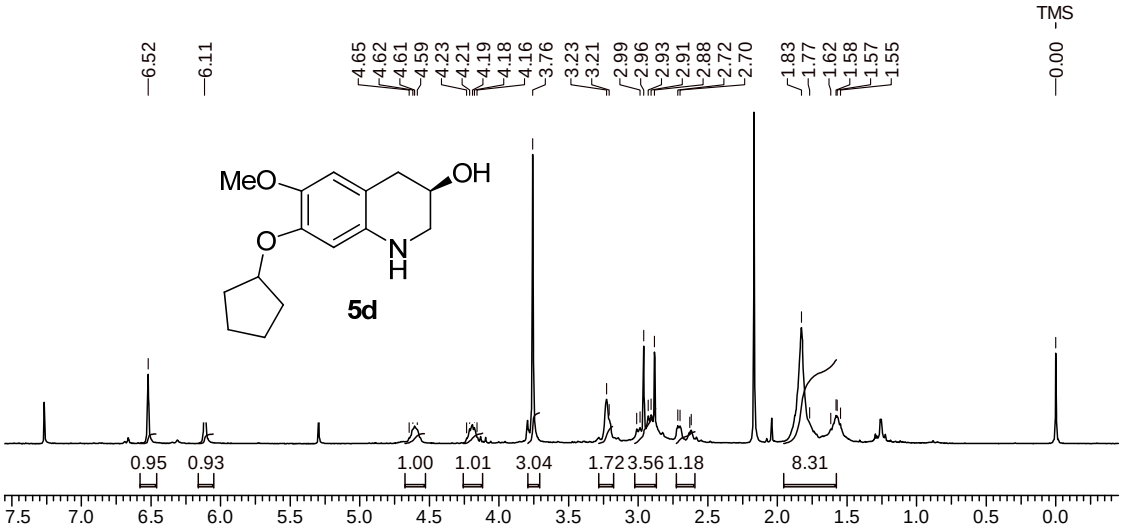
30.607	198857225	97.06	2598245	96.81
Totals	204883226	100.00	2683946	100.00

Figure 8: ^{1}H & ^{13}C NMR spectra and HPLC chromatogram of THQ **5c**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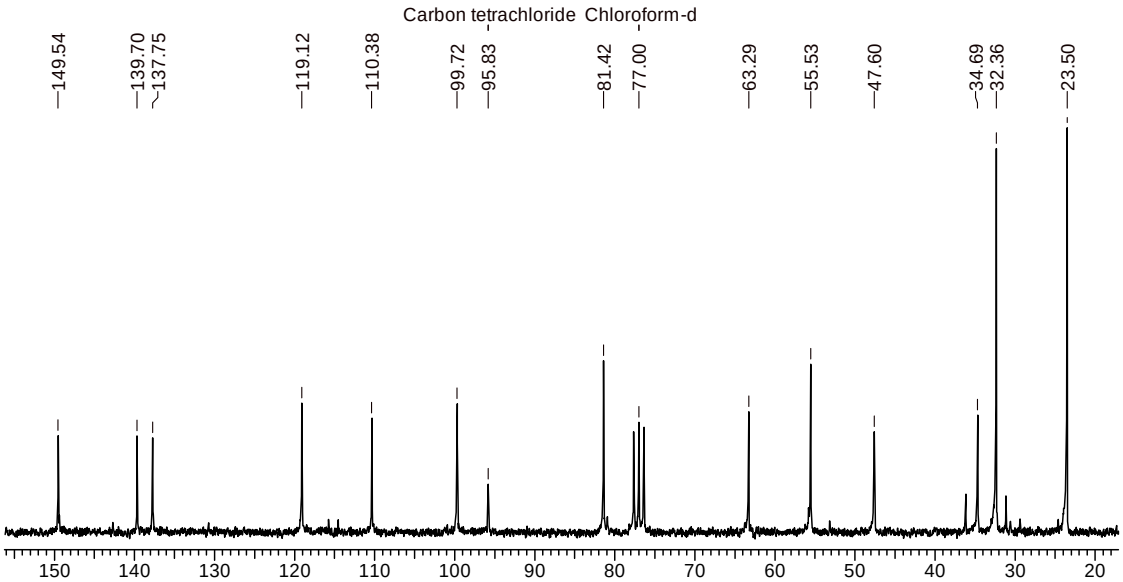
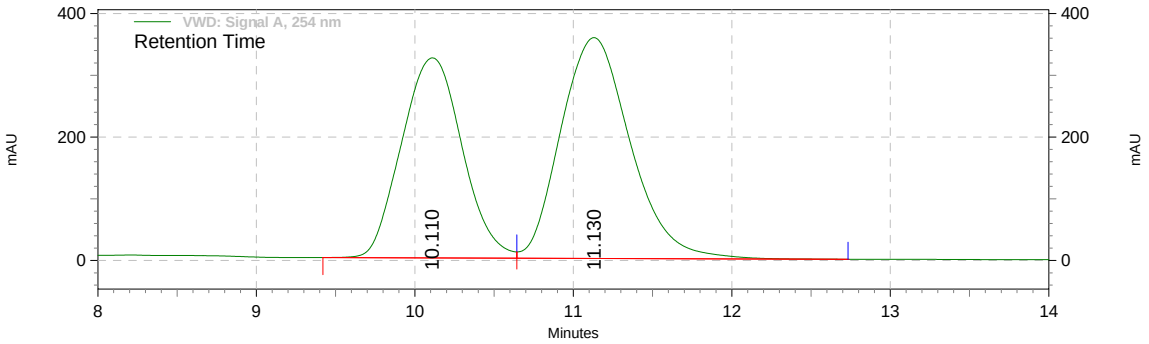
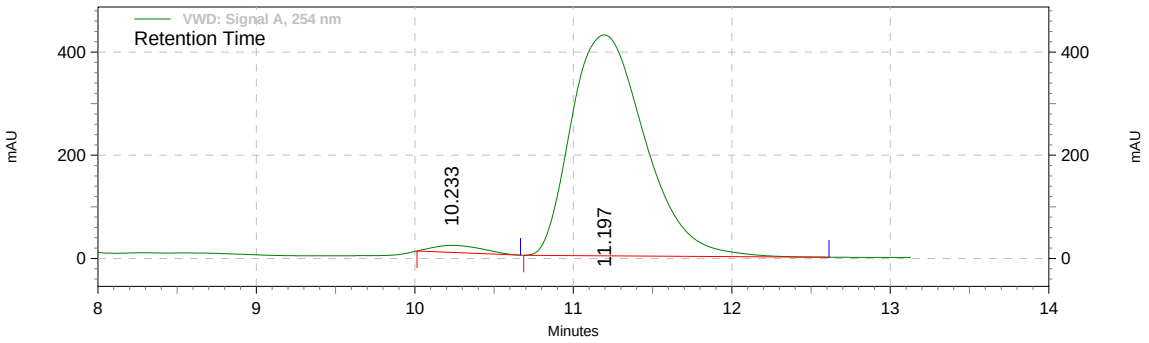
6.11
4.65
4.62
4.61
4.59
4.23
4.21
4.19
4.18
4.16
3.76
3.23
3.21
2.99
2.96
2.93
2.91
2.88
2.72
2.70
1.83
1.77
1.62
1.58
1.57
1.55
0.00
MeO
OH
O
N
H
5d
0.95
0.93
1.00
1.01
3.04
1.72
3.56
1.18
8.31
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0

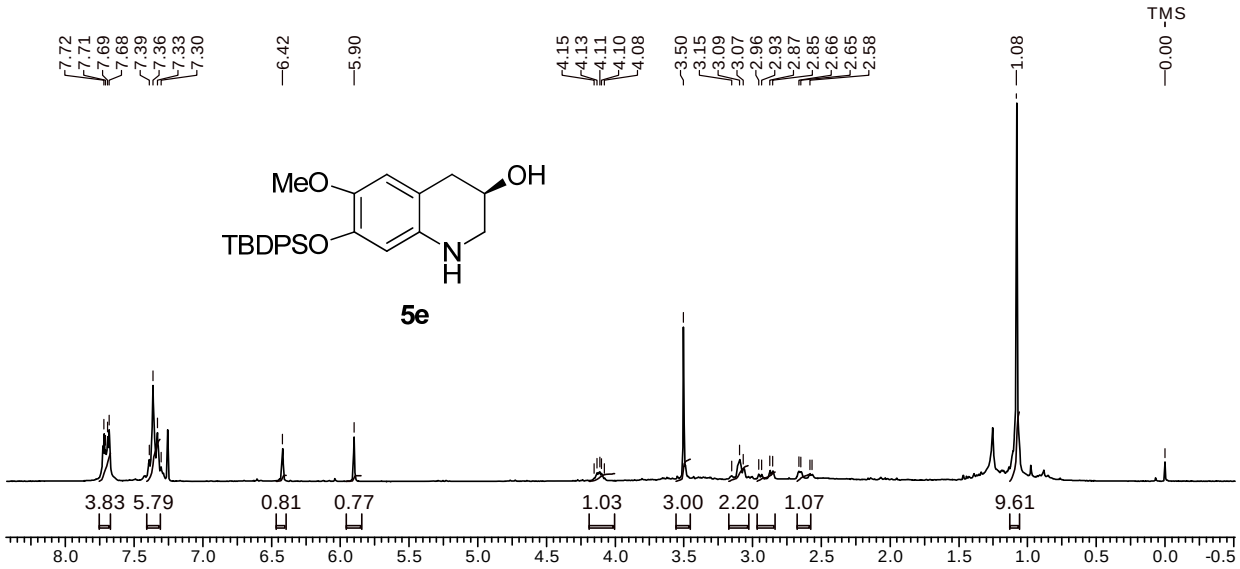

Carbon tetrachloride
Chloroform-d
149.54
139.70
137.75
119.12
110.38
99.72
95.83
81.42
77.00
63.29
55.53
47.60
34.69
32.36
23.50
150
140
130
120
110
100
90
80
70
60
50
40
30
20

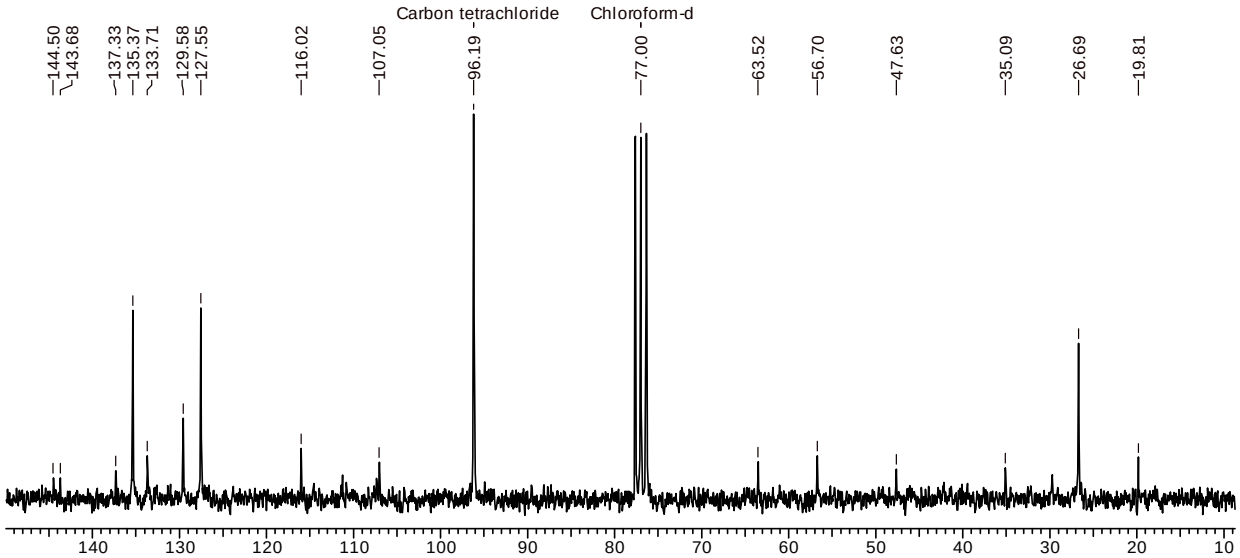

VWD: Signal A, 254 nm
Retention Time
mAU
400
200
0
10.110
11.130
8
9
10
11
12
13
14
Minutes

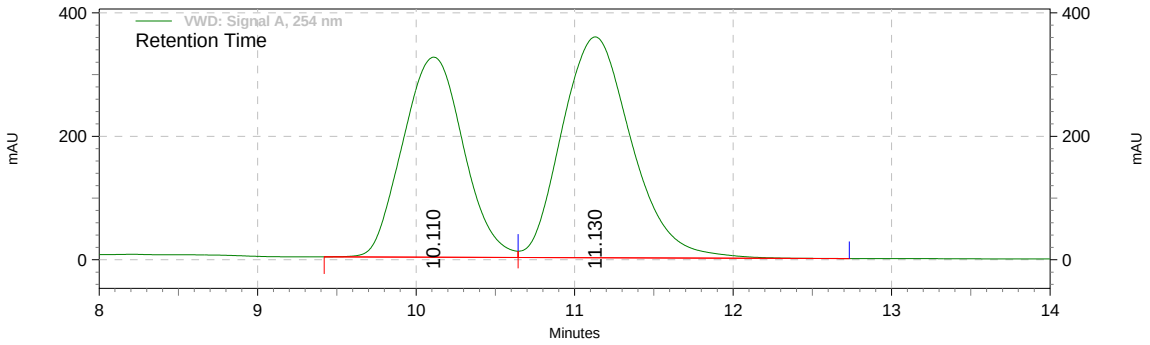


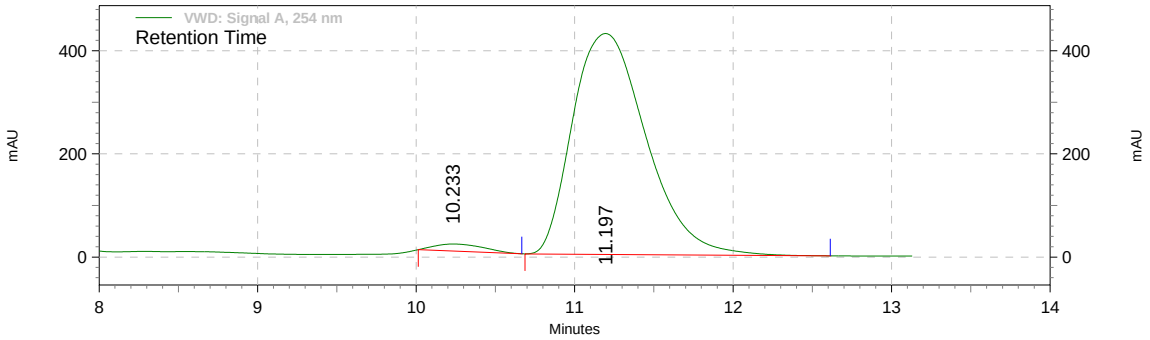
Retention Time	Area	Area %	Height	Height %
10.233	4980694	2.10	229461	3.10
11.197	231657212	97.90	7181886	96.90
Totals	236637906	100.00	7411347	100.00

Figure 9: ^{1}H & ^{13}C NMR spectra and HPLC chromatogram of THQ **5d**


TMS
7.72
7.71
7.69
7.68
7.39
7.36
7.33
7.30
6.42
5.90
4.15
4.13
4.11
4.10
4.08
3.50
3.15
3.09
3.07
2.96
2.93
2.87
2.85
2.66
2.65
2.58
1.08
0.00
MeO
OH
TBDPSO
N
H
5e
3.83
5.79
0.81
0.77
1.03
3.00
2.20
1.07
9.61
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5


Carbon tetrachloride
Chloroform-d
144.50
143.68
137.33
135.37
133.71
129.58
127.55
116.02
107.05
96.19
77.00
63.52
56.70
47.63
35.09
26.69
19.81
140
130
120
110
100
90
80
70
60
50
40
30
20
10





Retention Time	Area	Area %	Height	Height %
10.233	4980694	2.10	229461	3.10
11.197	231657212	97.90	7181886	96.90
Totals	236637906	100.00	7411347	100.00

Figure 10: ^{1}H & ^{13}C NMR spectra and HPLC chromatogram of THQ **5e**

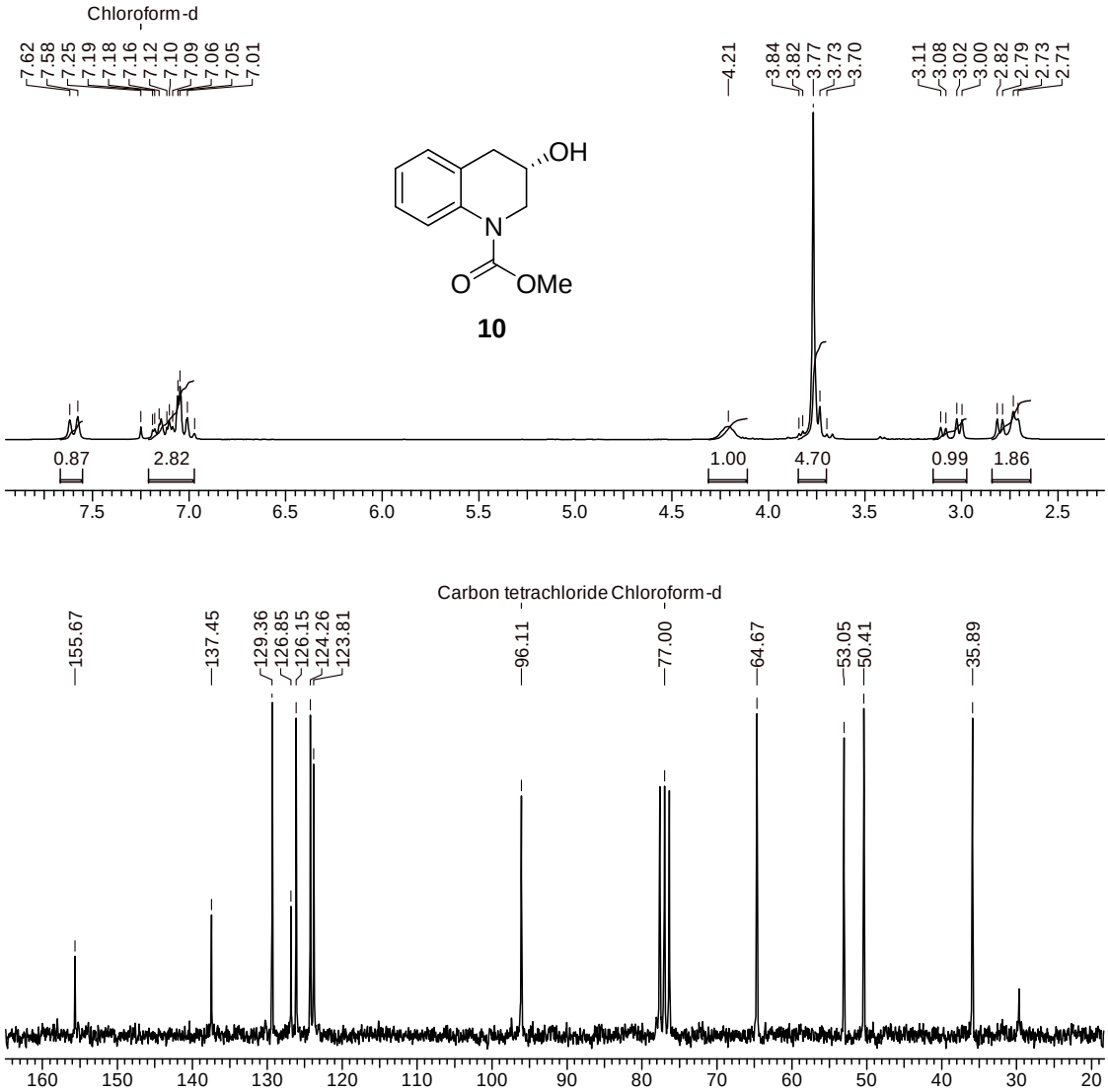


Figure 11: ^{1}H and ^{13}C NMR spectra of carbamate **10**

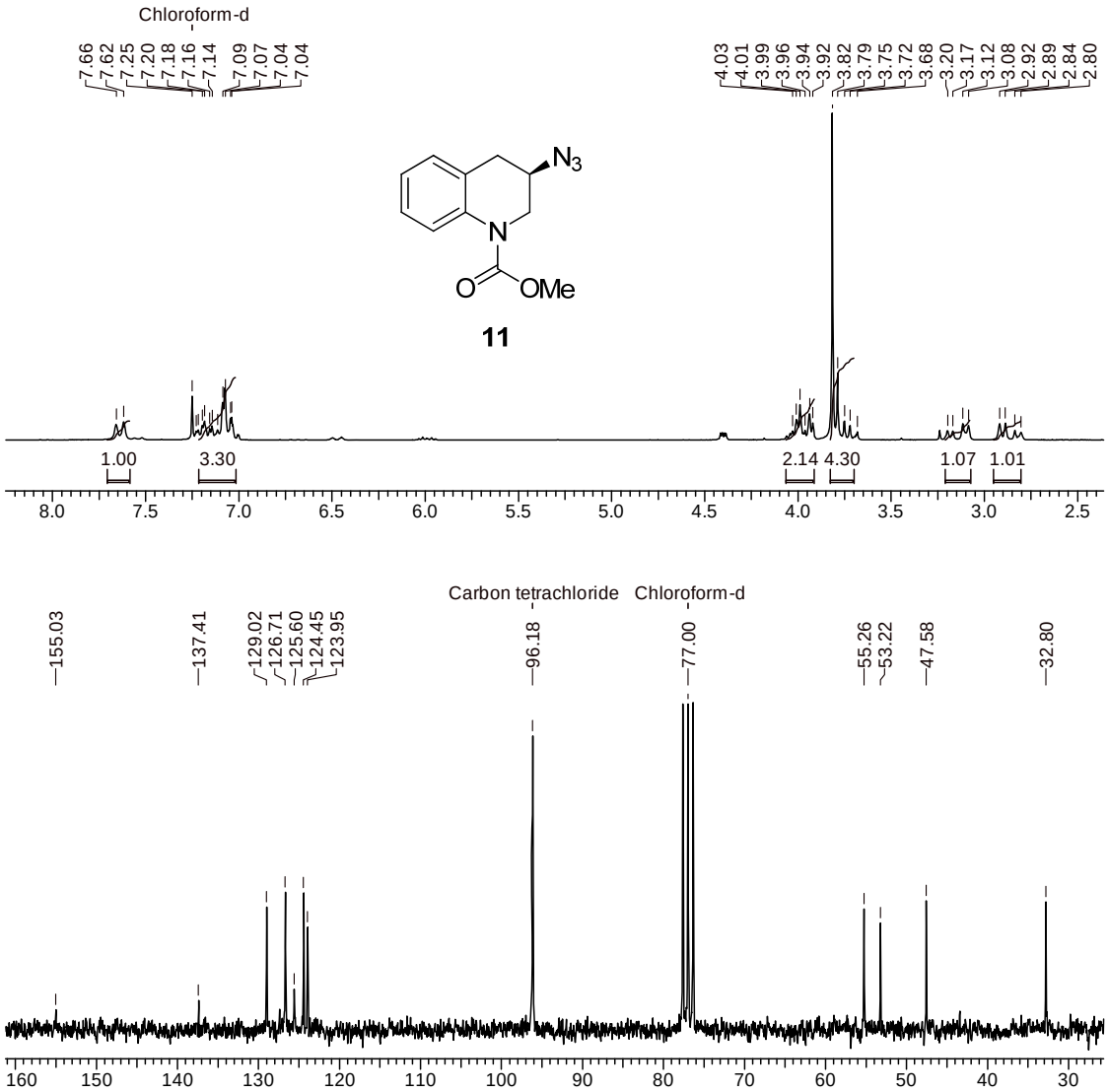


Figure 12: ^{1}H and ^{13}C NMR spectra of azide **11**

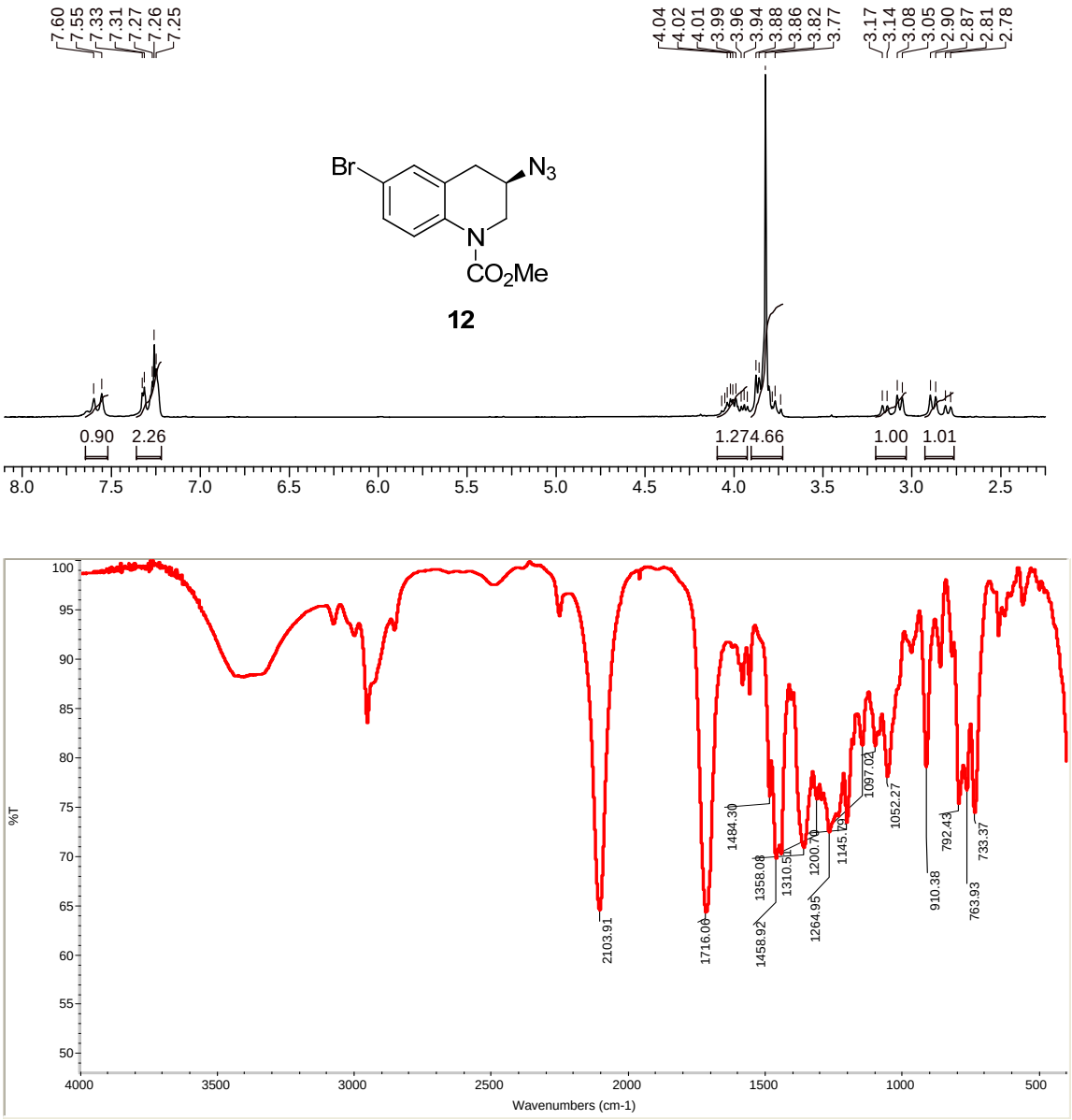


Figure 13: ^{1}H NMR and IR spectra of 6-bromo carbamate **12**

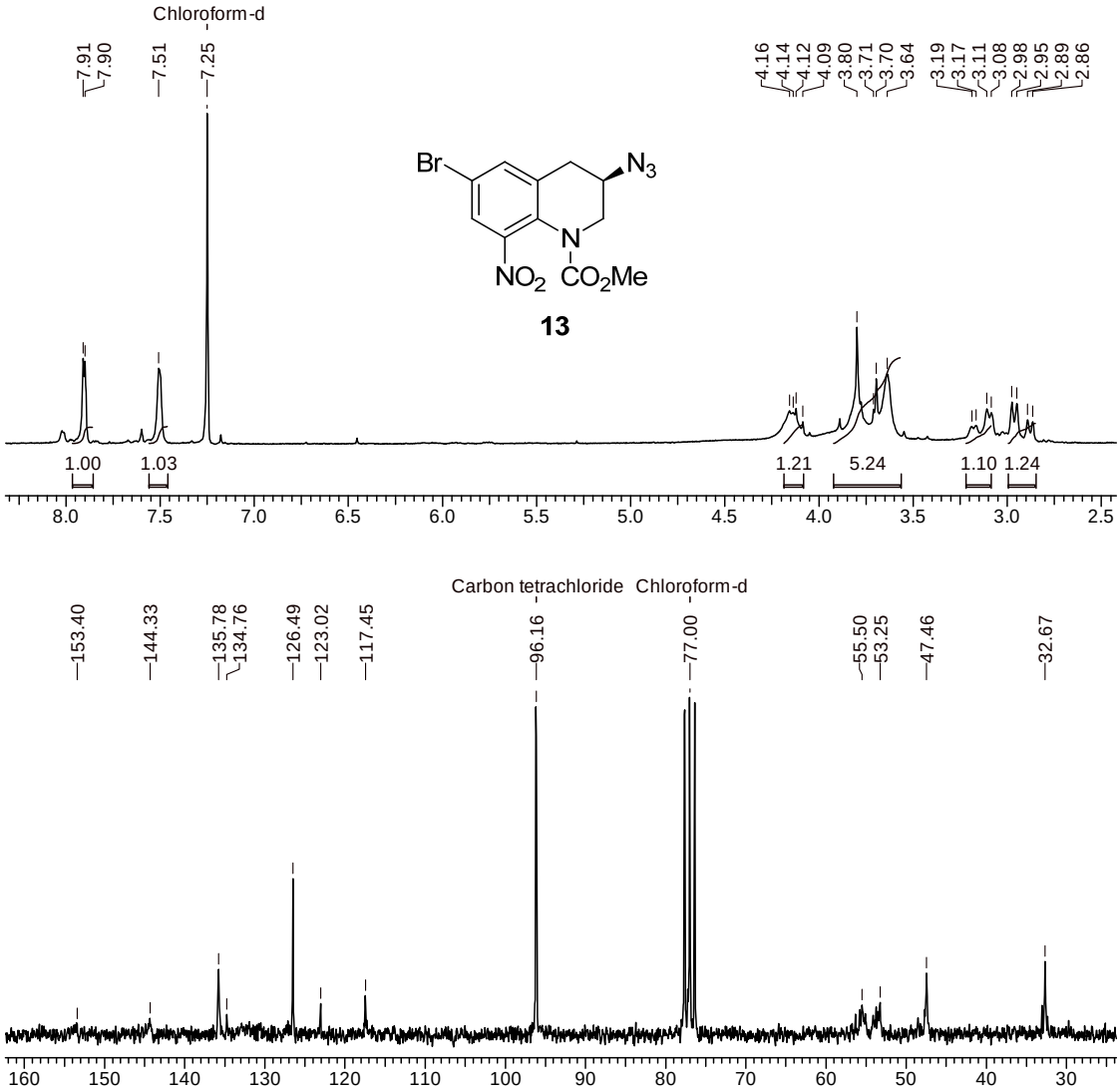


Figure 14: ^{1}H and ^{13}C NMR spectra of 6-bromo-8-nitro carbamate **13**

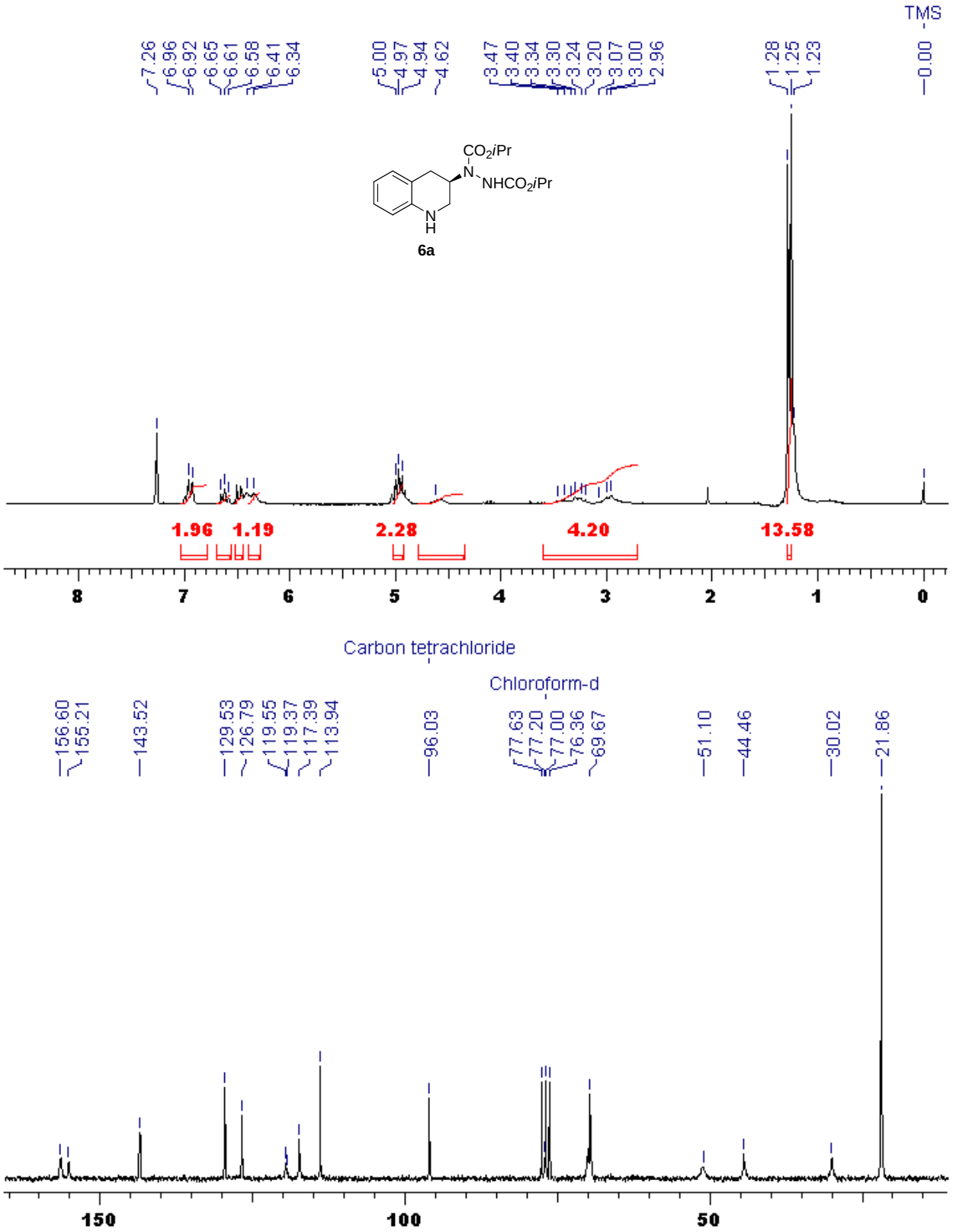


Figure 15: ^{1}H and ^{13}C NMR Spectra of **6a**

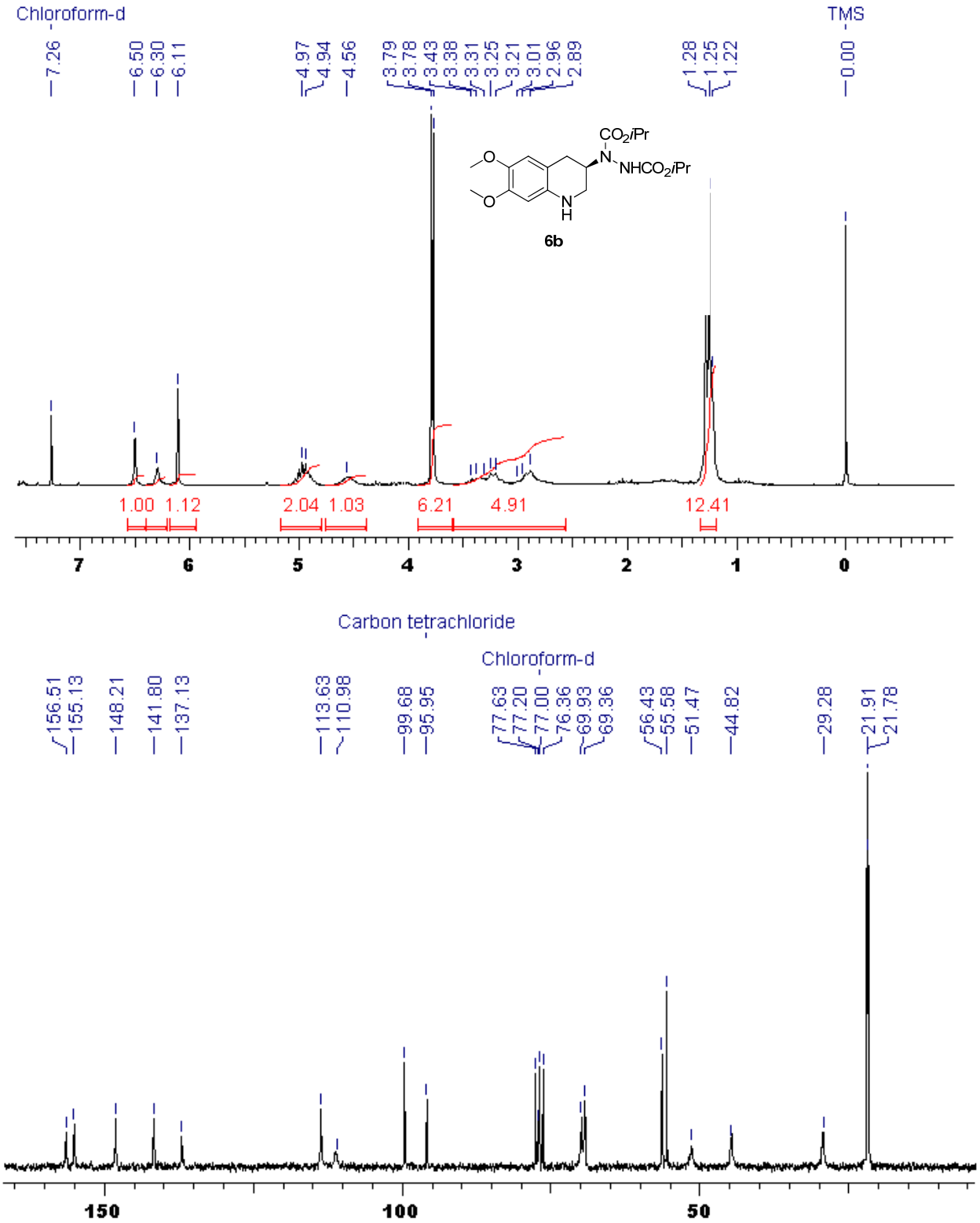
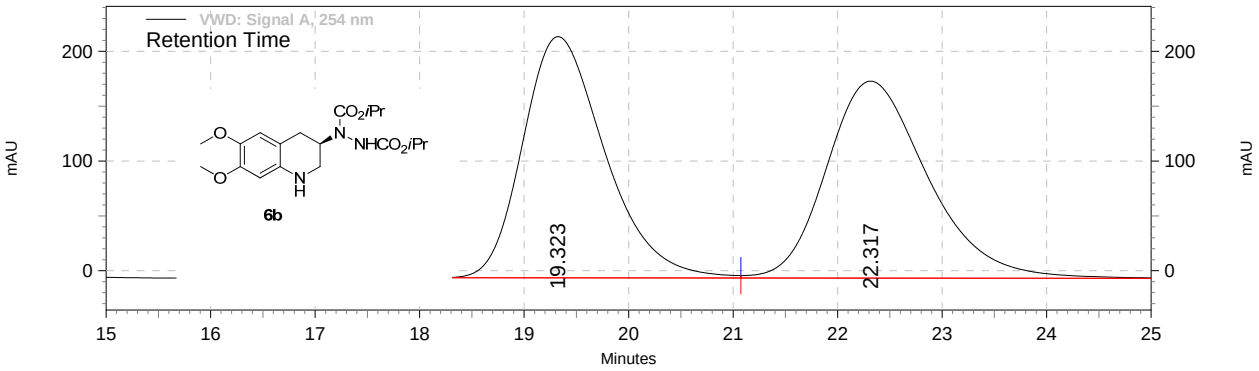
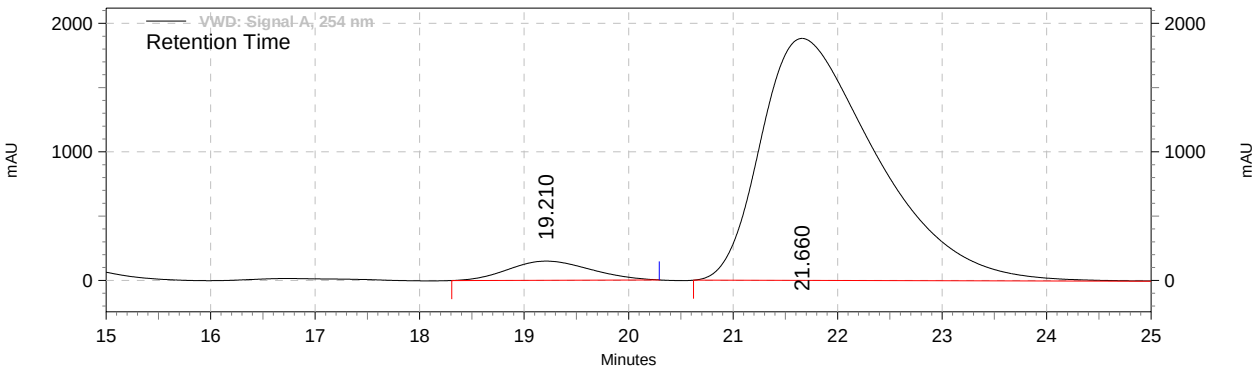


Figure 16: ^{1}H and ^{13}C NMR Spectra of **6b**





Retention Time	Area	Area %	Height	Height %
19.210	135951973	5.31	2499796	7.33
21.660	2422085955	94.69	31593077	92.67
Totals	2558037928	100.00	34092873	100.00

HPLC Chromatogram of **6b**

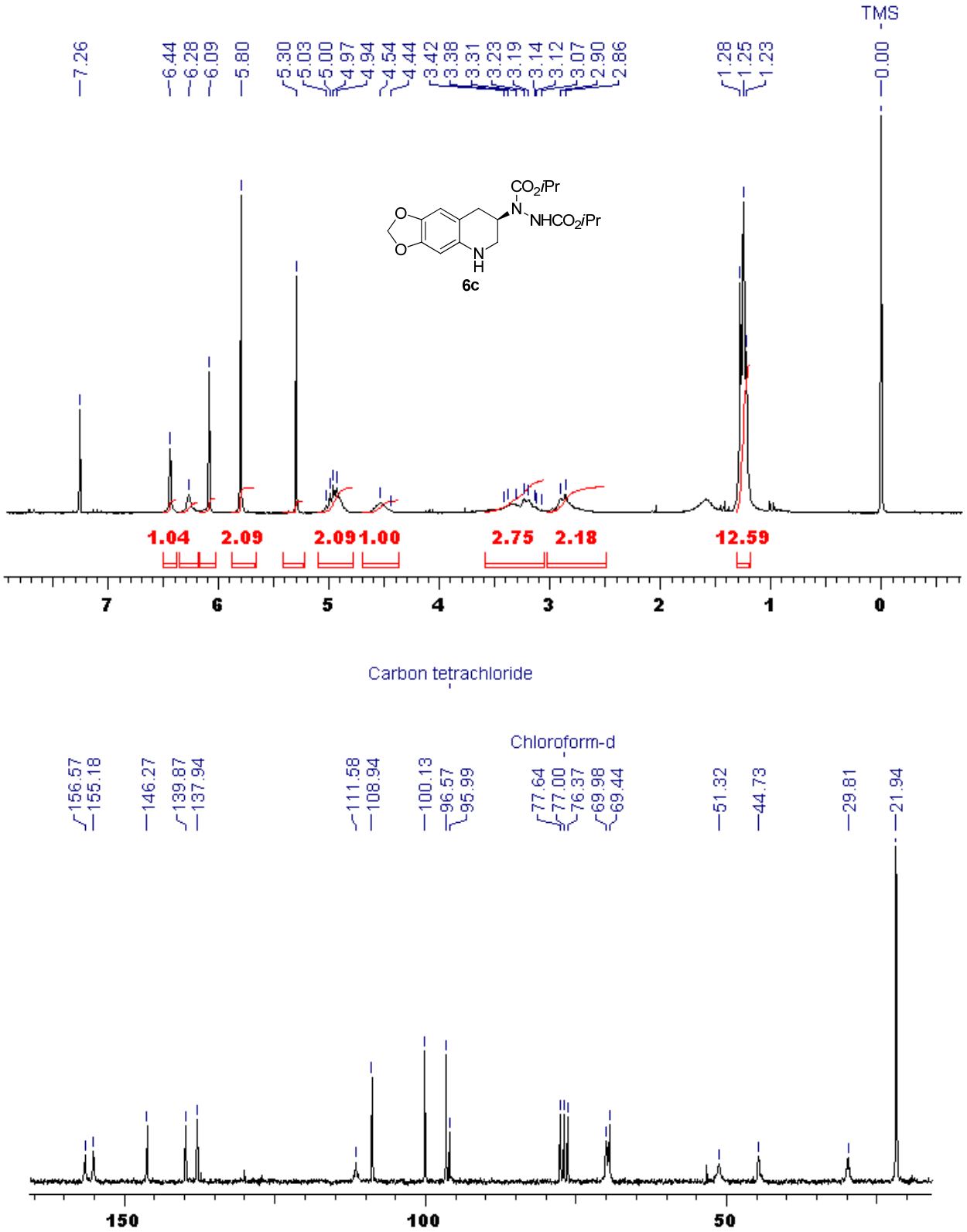


Figure 17: ^{1}H and ^{13}C NMR Spectra of **6c**

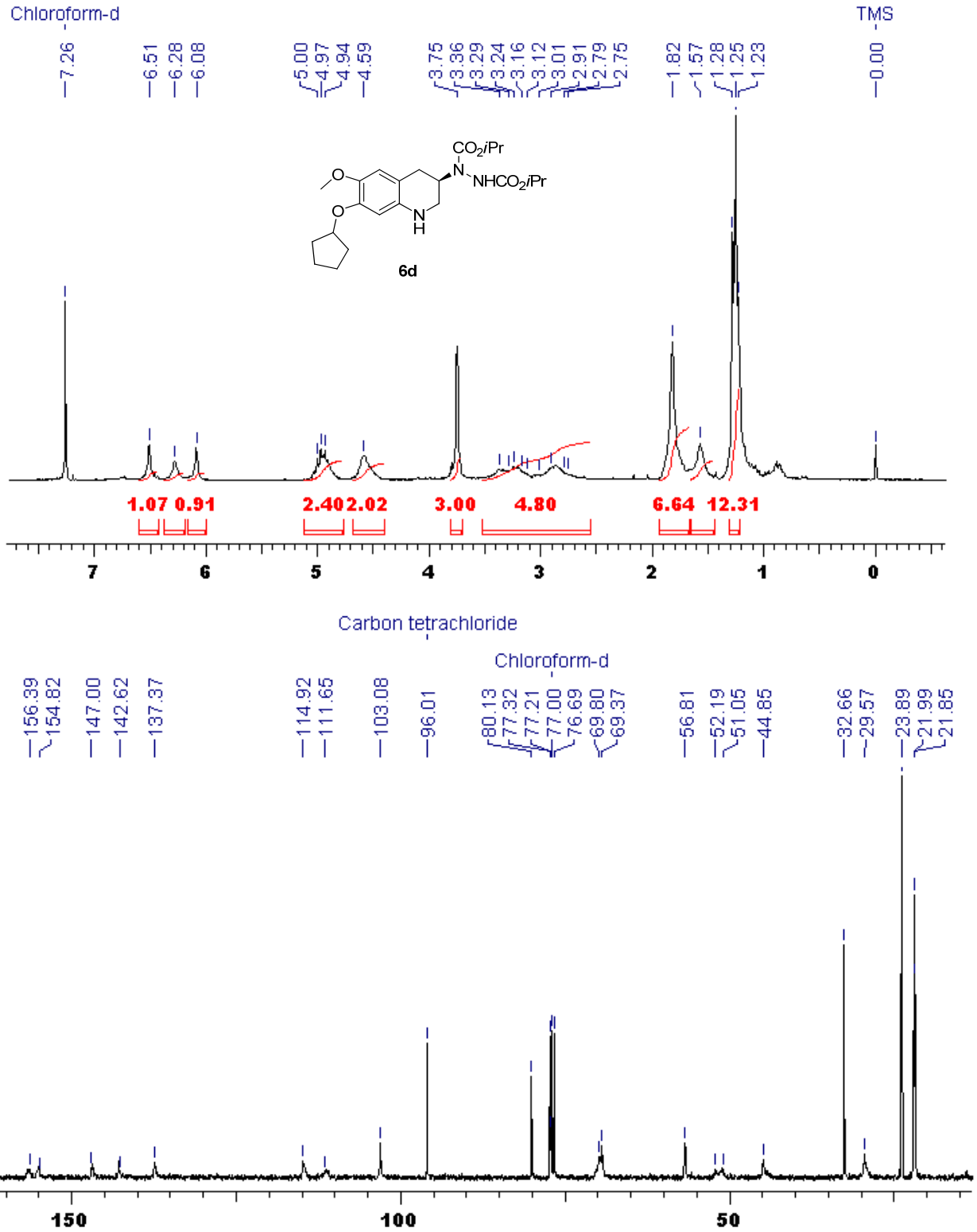
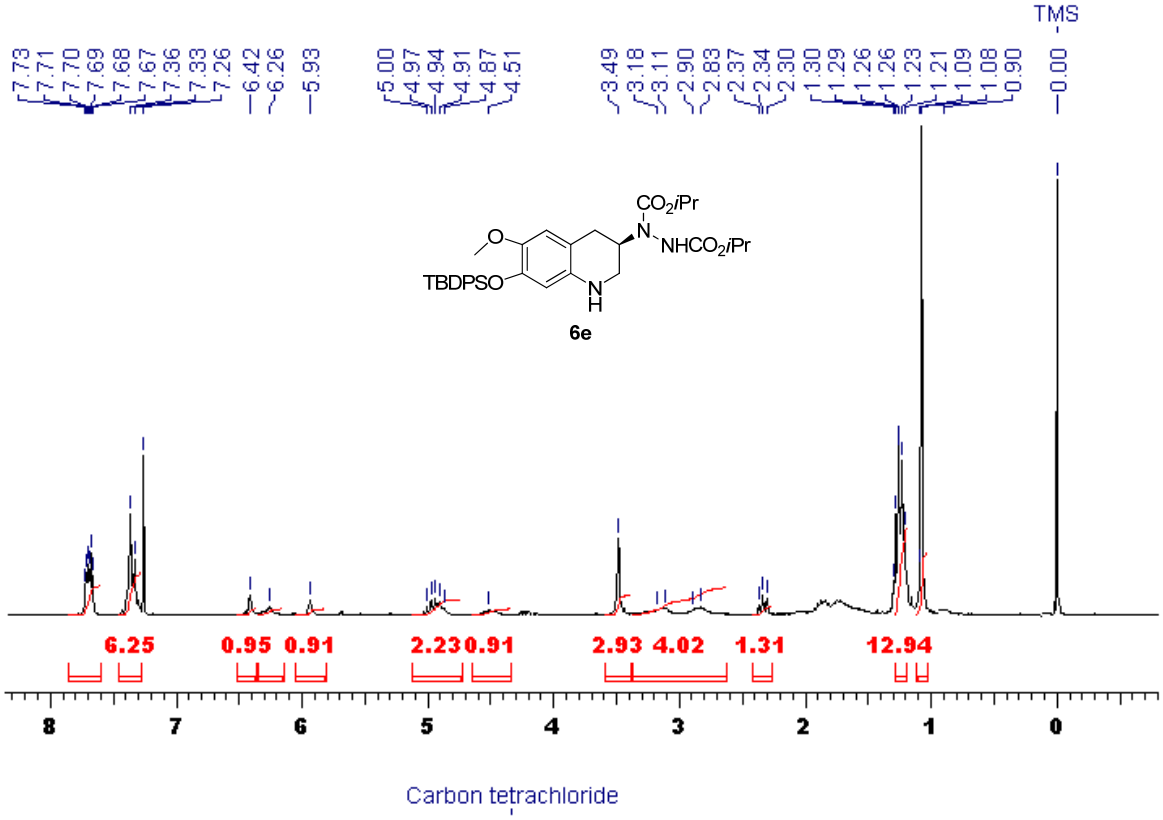


Figure 18: ^{1}H and ^{13}C NMR Spectra of **6d**



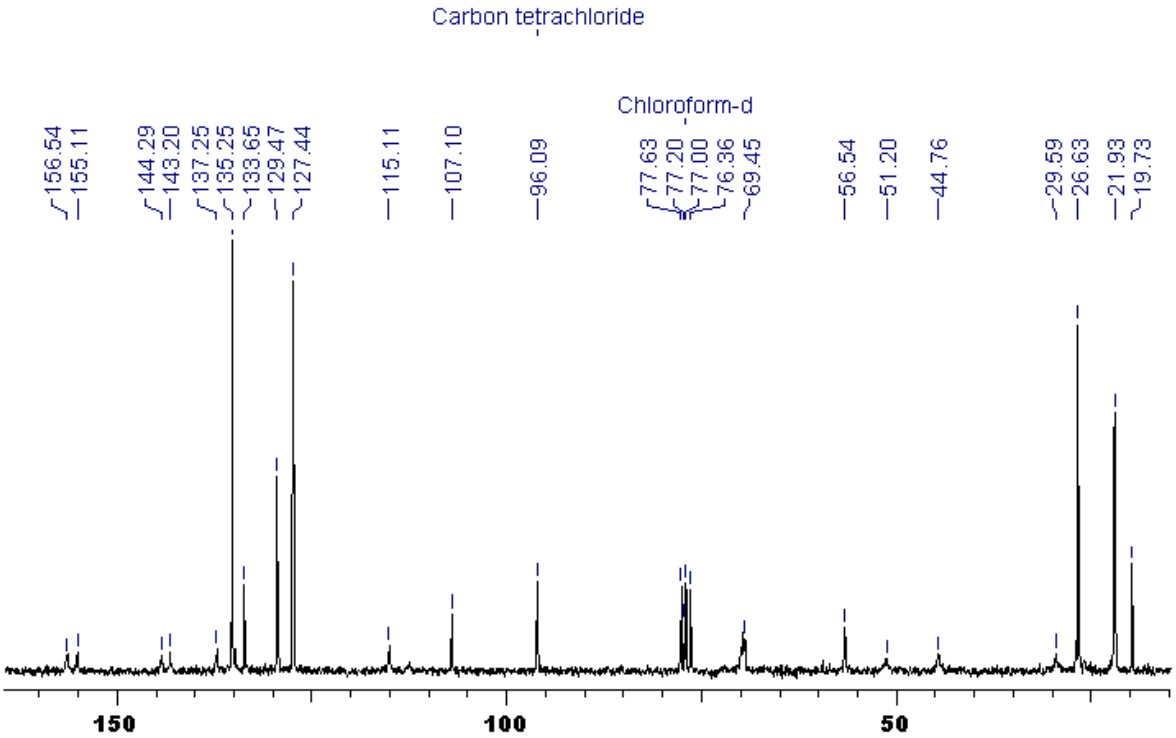


Figure 19: ^{1}H and ^{13}C NMR Spectra of **6e**

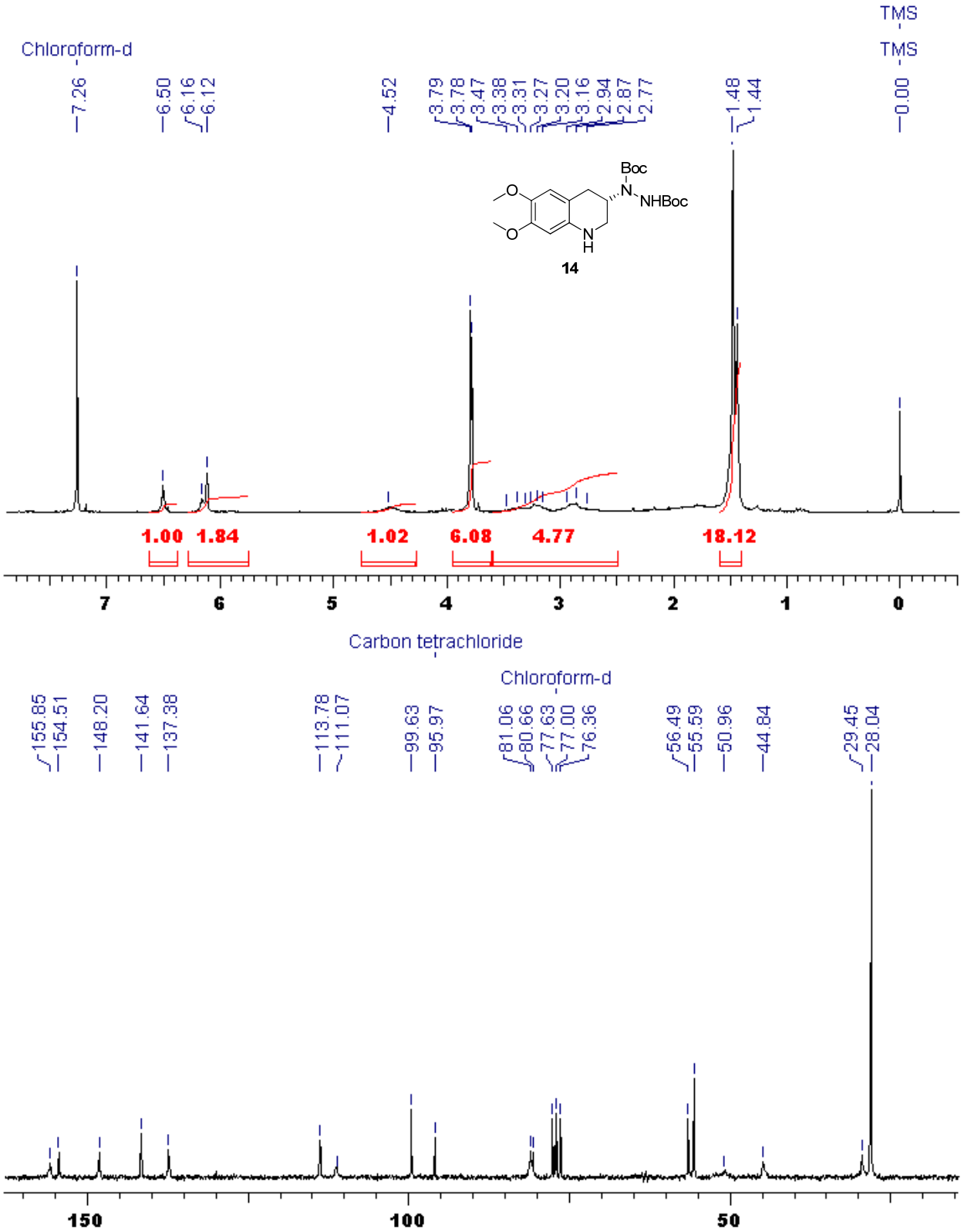


Figure 20: ^{1}H and ^{13}C NMR Spectra of **14**

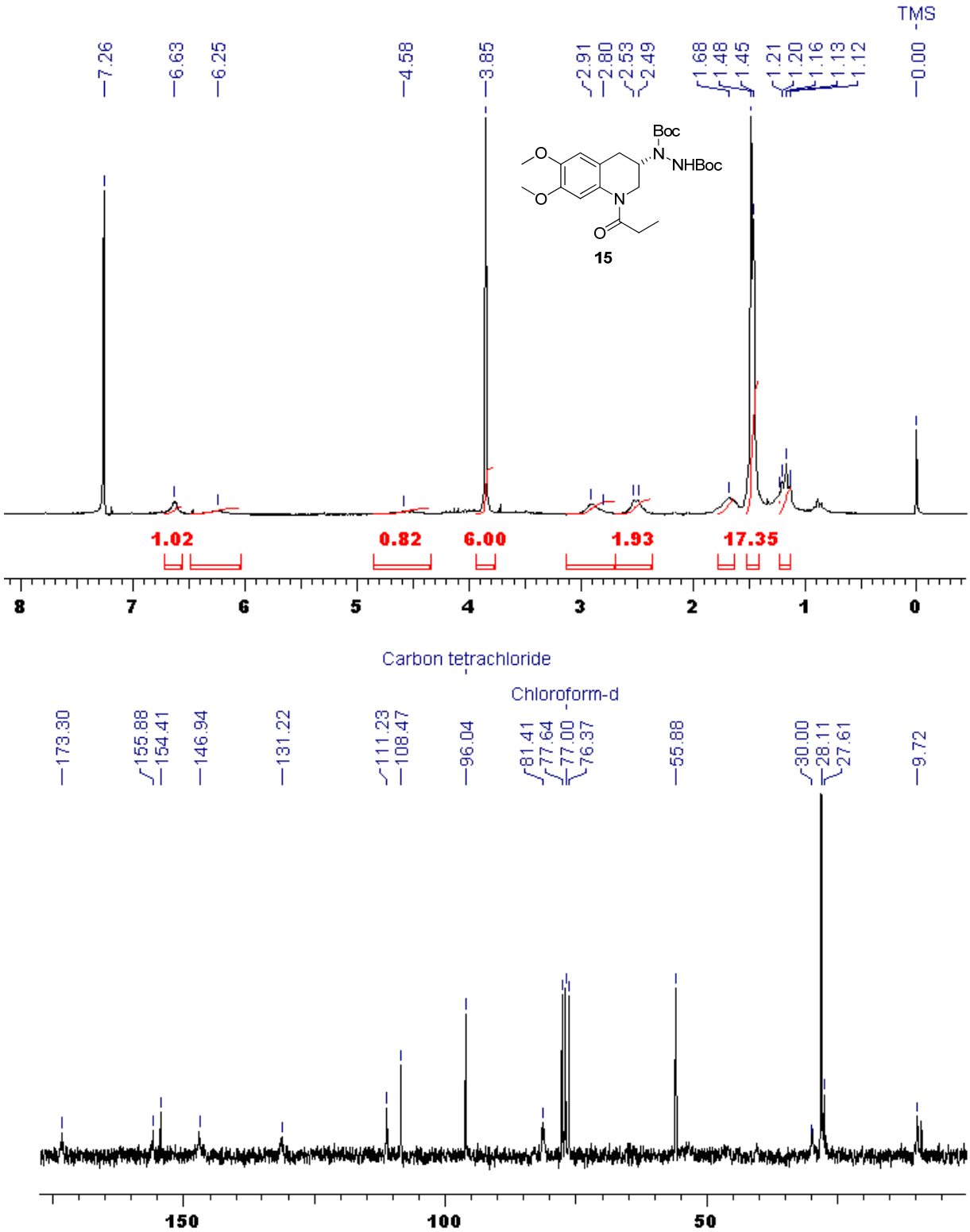


Figure 21: ^{1}H and ^{13}C NMR Spectra of **15**

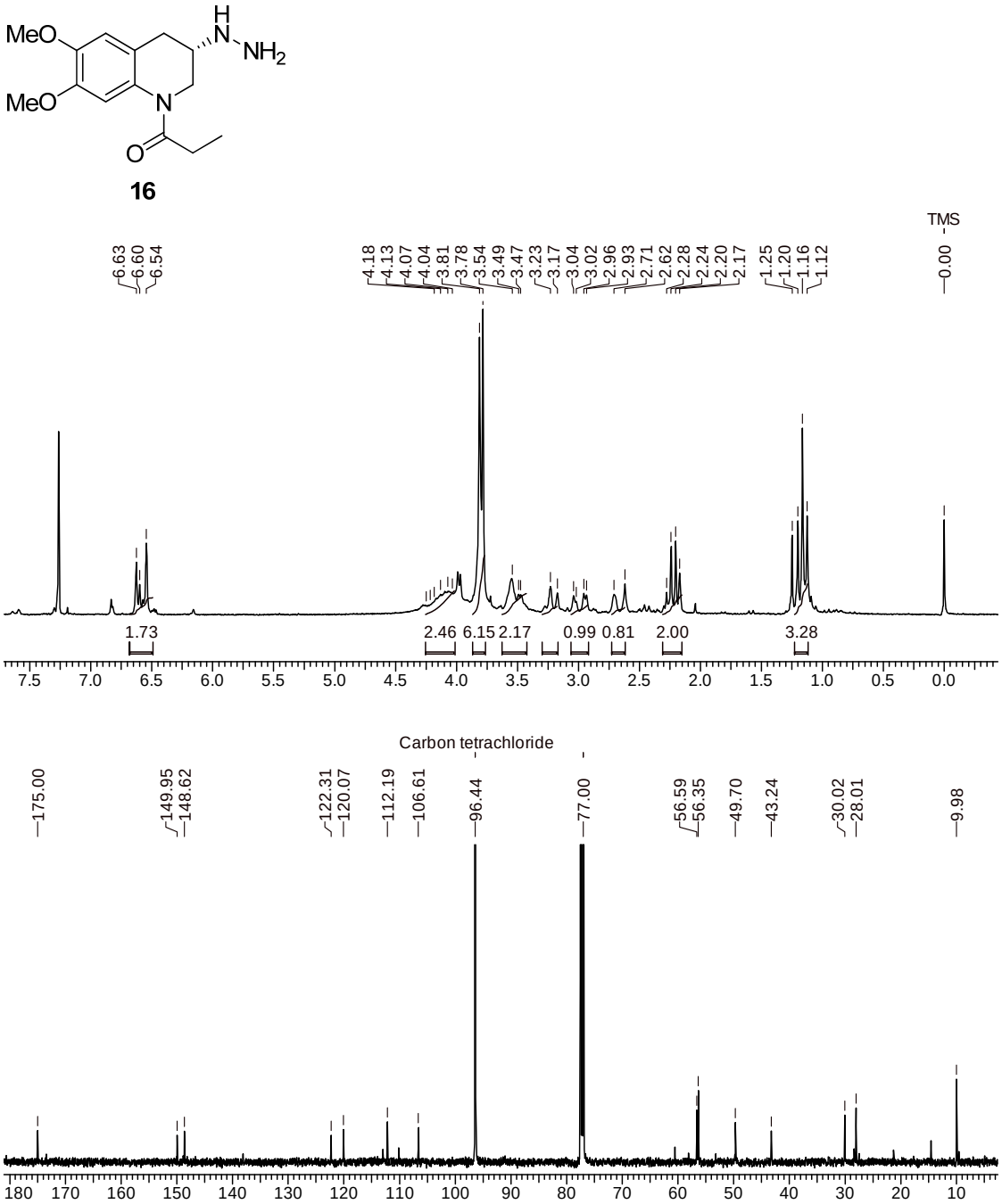


Figure 22: ^{1}H and ^{13}C NMR spectra of hydrazine **16**

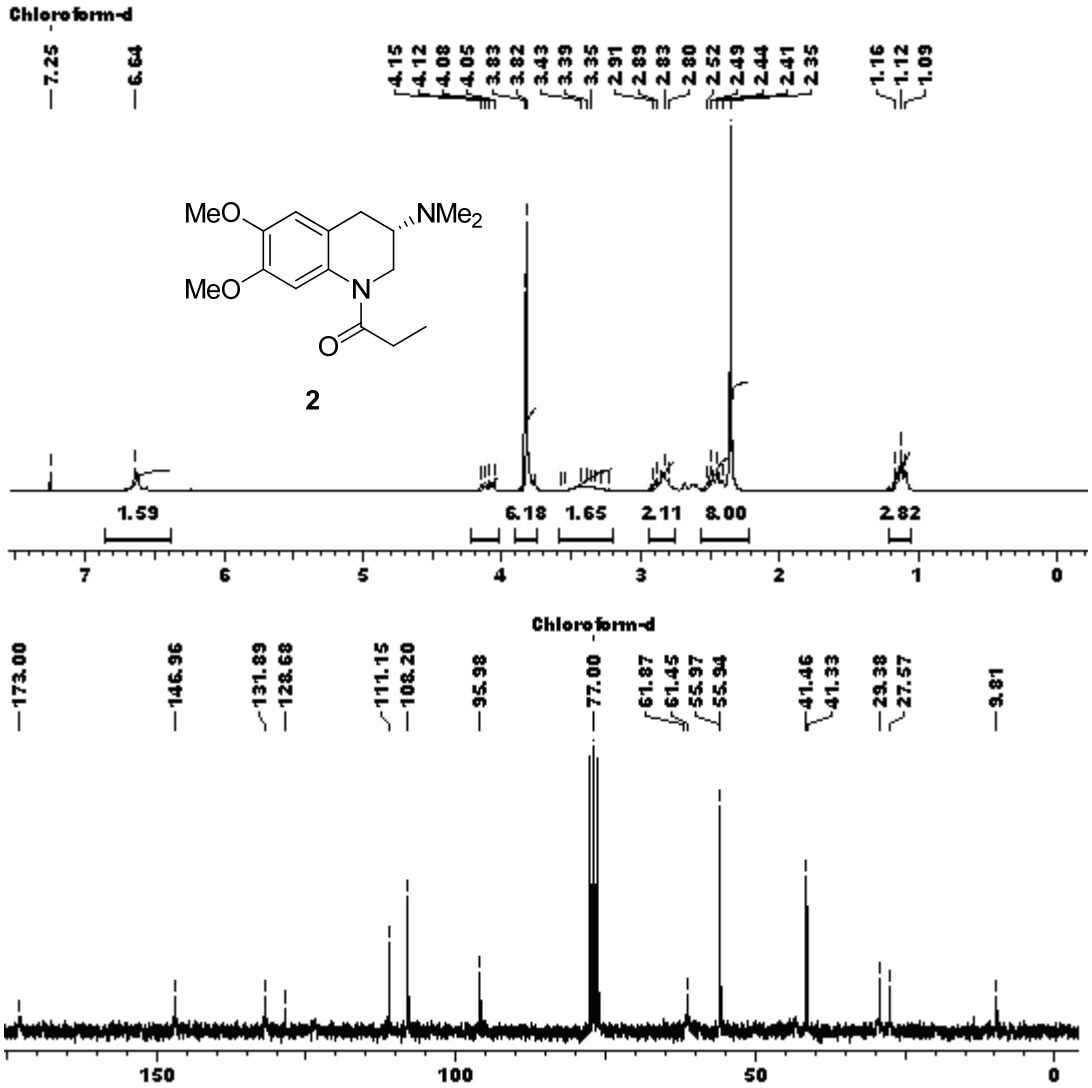
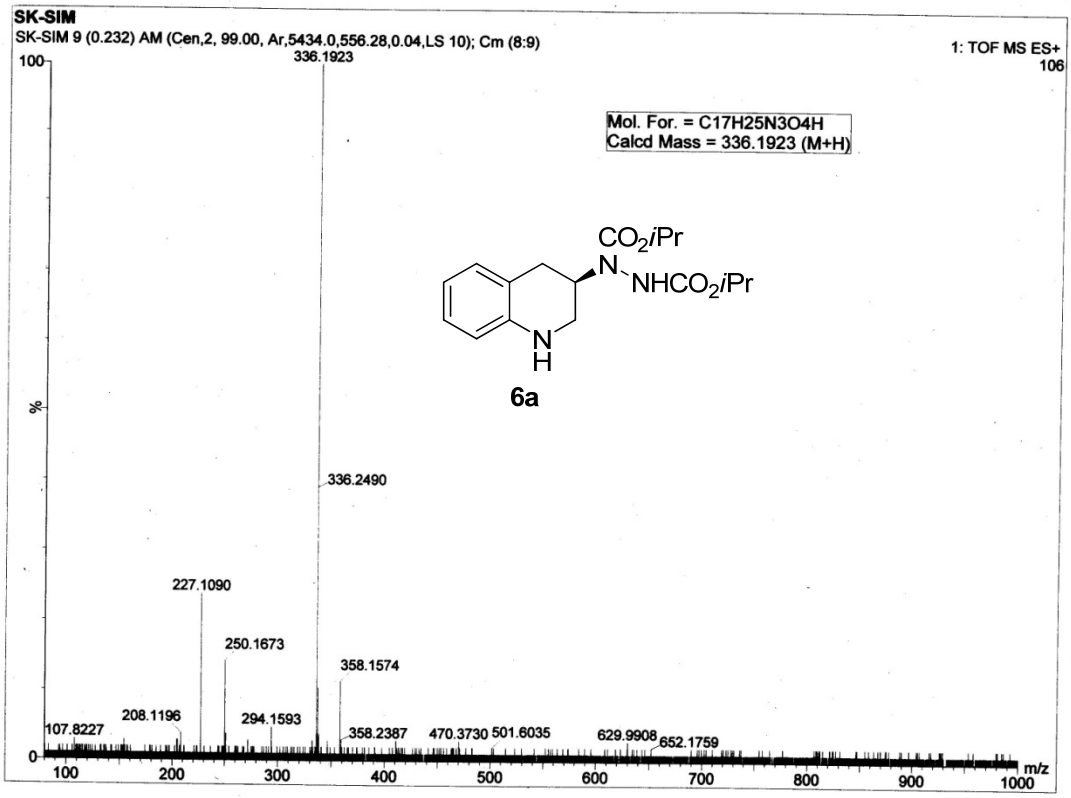
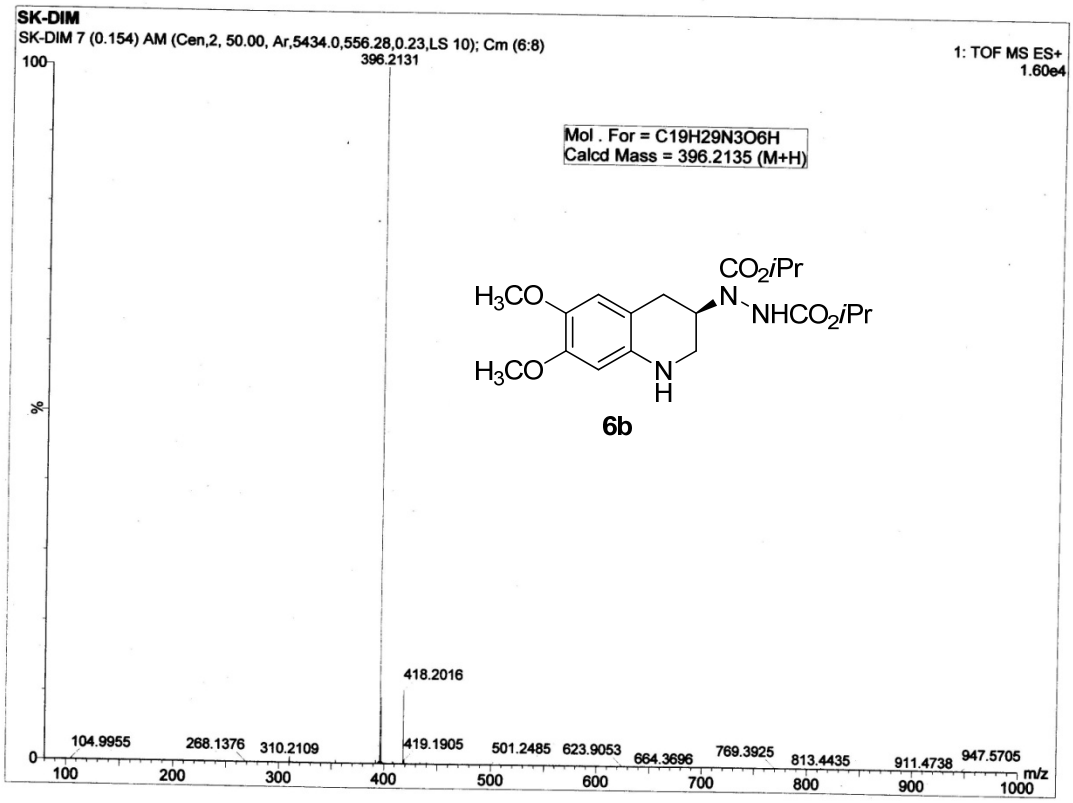
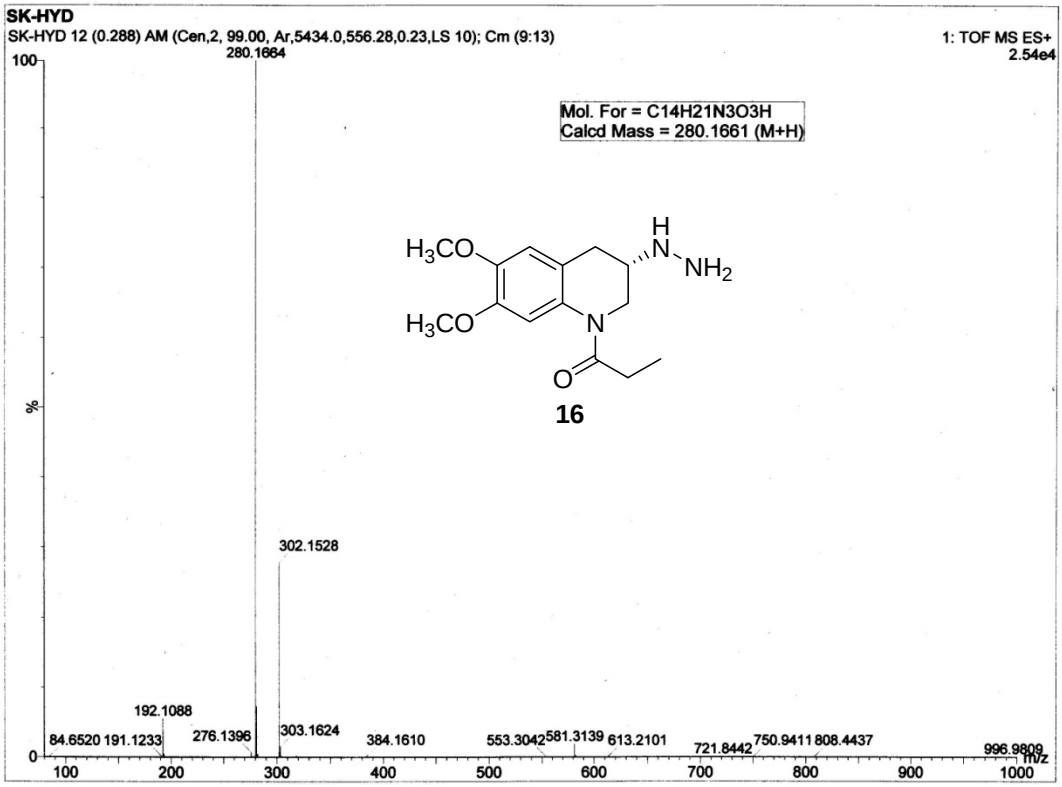


Figure 23: ^{1}H and ^{13}C NMR spectra of **2** (*S*)-903


SK-SIM
SK-SIM 9 (0.232) AM (Cen,2, 99.00, Ar,5434.0,556.28,0.04,LS 10); Cm (8:9)
1: TOF MS ES+
106
Mol. For. = C17H25N3O4H
Calcd Mass = 336.1923 (M+H)
CO2iPr
N
NHCO2iPr
N
H
6a
336.1923
336.2490
227.1090
250.1673
358.1574
208.1196
294.1593
107.8227
358.2387
470.3730
501.6035
629.9908
652.1759
100
%
0
100
200
300
400
500
600
700
800
900
1000
m/z


SK-DIM
SK-DIM 7 (0.154) AM (Cen,2, 50.00, Ar,5434.0,556.28,0.23,LS 10); Cm (6:8)
1: TOF MS ES+
1.60e4
Mol . For = C19H29N3O6H
Calcd Mass = 396.2135 (M+H)
396.2131
418.2016
104.9955
268.1376
310.2109
419.1905
501.2485
623.9053
664.3696
769.3925
813.4435
911.4738
947.5705
100
%
0
100
200
300
400
500
600
700
800
900
1000
m/z
H3CO
H3CO
CO2iPr
N
NHCO2iPr
N
H
6b


SK-HYD
SK-HYD 12 (0.288) AM (Cen,2, 99.00, Ar,5434.0,556.28,0.23,LS 10); Cm (9:13)
1: TOF MS ES+
2.54e4
Mol. For = C14H21N3O3H
Calcd Mass = 280.1661 (M+H)
H3CO
H3CO
H
N
NH2
N
O
16
280.1664
302.1528
192.1088
84.6520
191.1233
276.1396
303.1624
384.1610
553.3042
581.3139
613.2101
721.8442
750.9411
808.4437
996.9809
100
%
0
100
200
300
400
500
600
700
800
900
1000
m/z